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Gasoline Alley, Fort Drum Bioremediation Evaluation, Area 1795, Phase I and Phase II

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Herbert Fredrickson, Roy Wade, Rakesh Bajpai,
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Preface

The study herein was conducted as a part of a site remediation of total petroleum hydrocarbon at Area 1795 located along Gasoline Alley at an active military installation of Fort Drum, New York. This report was prepared at the U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, in cooperation with the Fort Drum Military Installation, New York, New York State Department of Environmental Control, and the U.S. Army Engineer District (USAED), Baltimore. Program Manager for Fort Drum was Ms. Ann Wood. Program Manager for USAED, Baltimore, was Ms. Shelley Spayde. Project Managers for ERDC were Mr. Jeffrey Talley, Environmental Laboratory (EL), ERDC, and Dr. Rakesh Bajpai, University of Missouri, Columbia, and Principal Investigators for ERDC were Messrs. Lance Hansen and Roy Wade, EL, ERDC.

The bench-scale studies were conducted between March 1997 and October 1997 at the ERDC, EL. This report was written by Mr. Scott Waisner, AScl, ERDC contractor; Messrs. Lance Hansen, Jeffrey Talley, and Roy Wade, Environmental Restoration Branch (ERB), Environmental Engineering Division (EED), Dr. Herbert Fredrickson and Mr. David Ringelberg, Ecosystem Processes and Effect Division (EPED), EL, ERDC; and Dr. Bajpai.

The report was prepared at ERDC under the direct supervision of Mr. Daniel E. Averett, Chief, ERB, and under the general supervision of Dr. Richard Price, Chief, and Dr. John Keeley, Acting Director, EL.

At the time of publication of the report, Director of ERDC was Dr. James R. Houston, and Commander was COL James S. Weller, EN.

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Executive Summary

The goal of this effort was the evaluation biotreatability options for total petroleum hydrocarbons (TPH) contaminated Area 1795 located along Gasoline Alley at the active duty military installation of Fort Drum, New York. Area 1795 most recently contained two 94,600-ℓ (25,000-gal) and one 45,600-ℓ (12,000-gal) steel underground storage tanks (USTs) used for refueling military vehicles with unleaded gasoline and was part of a nine-site refueling complex containing 21 USTs. The objectives of the evaluation were to: (a) determine potential microbial activity of Area 1795 subsurface soils; (b) determine intrinsic TPH degradation potential of Area 1795 subsurface microorganisms; (c) determine parameters which will enhance subsurface microbial growth in Area 1795; (d) optimize parameters using column study simulation of Area 1795 subsurface conditions; and (e) generate data for design and preliminary cost evaluation for the remediation of Area 1795.

Microcosm Studies

Initially, a single 5-m (15-ft) core was taken near well MWS6 from Area 1795 to a depth of 5 m (15 ft). This core traversed the anticipated area of the smear zone. From this core, subsurface contaminant and microbial profiles were developed for Area 1795. Following characterization, soil aliquots from the top and bottom of the smear zone were challenged with radiolabeled acetate in respirometry flask studies to determine the basal microbial activity of Area 1795 subsurface soils. Acetate was chosen for this challenge because it can be easily utilized as a source of energy and/or carbon by most microorganisms. These studies were conducted under unsaturated and saturated conditions to simulate the vadose and saturated zones in the aquifer during seasonal fluctuations. It was determined through the microbial profile and flask studies that the subsurface of Area 1795 contained a healthy and diverse population of microorganisms with a significant metabolic potential, specifically immediately above the area of significant TPH contamination that was seen in the core.

Following the acetate challenge, Area 1795 soils were challenged with radiolabeled phenanthrene in respirometry flasks. Phenanthrene was chosen to estimate the intrinsic TPH degradation potentials of the native microorganisms. Phenanthrene is a relatively recalcitrant compound compared with other fuel range hydrocarbons, and as such, phenanthrene degradation results will represent conservative estimates of overall microbial activity on bulk hydrocarbon contamination. The experimental control, exposed only to atmospheric air, resulted in the highest metabolism of the tracer compound. This evaluation indicated that amendments other than molecular oxygen were not necessary to mineralize the recalcitrant contaminant. This suggests that molecular oxygen

from atmospheric air is a sufficient amendment to stimulate microbial degradation of hydrocarbon contamination in the subsurface of Area 1795.

Column Studies

Following respirometry flask studies, three additional 5-m (15-ft) subsurface cores were extracted from Area 1795 in July 1997. These cores were extracted within a 3-m (10-ft) radius of the core extracted in March 1997. The final phase of the study consisted of using these cores in packed soil columns operated in parallel. The soil columns were used to compare three alternatives for the remediation of Area 1795: natural attenuation (NA), bioventing (BV), and biosparging (BS). Soil, water, and vapor samples were analyzed over the course of the evaluation. Independent analysis and comparison of each phase were completed and compared among competing alternatives.

Samples were collected from various sampling ports at approximately 2-week intervals following a 3-day equilibration period. Soil samples were taken from ports throughout the column. Water samples were taken from the three lowest ports of the columns and represented three groundwater zones in the vertical groundwater profile. At each sampling event, all free water was removed from the column and replaced with contaminated groundwater from the site. Off gases from the columns were analyzed daily for concentrations of oxygen and carbon dioxide. These gases were also checked for petroleum hydrocarbons several times during the evaluation. The columns were sacrificed after 10 weeks, and the soil samples were analyzed for recoverable total petroleum hydrocarbon (rTPH) and microbial phospholipid fatty acids (PLFA).

Initial rTPH and microbial analysis of cores showed a similar vertical contaminant distribution pattern in the cores, but absolute contaminant concentrations differed significantly between cores. rTPH contamination was present predominantly on the soil and limited primarily to the lower half of the column. Water phase rTPH concentrations increased in the upper saturated zone of the bioventing and biosparging columns after the initial 3-day equilibration, confirming that the soil continues to act as a source of contamination. Maximum increases in aqueous-phase rTPH concentrations occurred near the smear zone where soil-phase rTPH concentrations were the highest.

Analyses of soil data suggested that the changes in soil TPH concentrations over the 9 1/2-week evaluation were significant (above the 95 percent confidence level) for the bioventing and biosparging treatment conditions. The significance of the change of total TPH contamination in the natural attenuation treatment condition could only be seen at the 92 percent confidence interval. The zero-order removal rate of rTPH was 2.5, 17.5, and 12.9-mg rTPH kg contaminated soil⁻¹ day⁻¹ for the natural attenuation, bioventing, and biosparging columns, respectively.

An analysis of pore water data suggests that active aeration increased the rate of TPH removal from the aqueous phase. The first-order removal-rate constants

were 2.65 and 1.82 day⁻¹ for the bioventing and biosparging columns, respectively. These removal-rate constants suggest that both bioventing and biosparging will reduce the extent of TPH migration in the groundwater.

Independent confirmations of rTPH biodegradation in the soils were obtained for bioventing and biosparging columns through the analyses of exit gas data. The exit gas analyses showed production of carbon dioxide at the expense of oxygen in the gas phase (evidence of aerobic metabolism). Respiration coefficients (RQ – ratio of carbon dioxide production to oxygen consumption) of approximately 0.8 were observed which indicates the aerobic metabolism of reduced organics such as hydrocarbons. Further more, the respiration activity was sustained throughout the experiment. These data suggest that metabolization of petroleum hydrocarbons in the bioventing and biosparging columns was taking place at the respective steady rates of 0.27- and 0.88-mg rTPH/kg contaminated soil/day. These steady rates were witnessed with an airflow rate of 1 sccm (standard cubic centimeter per minute) in each column. This corresponds to specific flow rates of 49-scc air/kg soil/day in the bioventing column and 51-scc air/kg soil/day in the biosparging column. The average linear velocity of air in each column was 5.6 cm/hr.

Bioventing resulted in the most significant removal rate of rTPH in the soil but biosparging showed evidence of the highest biological degradation rate of TPH. The most significant TPH removal in the bioventing and biosparging columns appears to be through volatilization.

1 Introduction

The U.S. Army Engineer Research and Development Center (ERDC), Vicksburg, MS, under scope of work agreement with the U.S. Army District (USEAD), Baltimore, conducted a biological treatability study to evaluate three alternative remediation strategies and provide information useful for the design and implementation of long-term remediation activities for Area 1795 of Gasoline Alley, Fort Drum, New York. The project was executed between March 1997 and October 1997. This document reports final analysis of treatability evaluations for Area 1795.

Objectives

The intent of this study was to provide Hazardous, Toxic, Radioactive Waste (HTRW), USAED, Baltimore, and Fort Drum Environmental Public Works, with site-specific information relevant to alternative remediation technologies that is useful in making informed engineering decisions for follow-on remediation activities. To meet this intent, a two-phase treatability study was conducted. Phase I consisted of microcosm evaluations using a single soil core collected in March 1997. Phase II consisted of a side-by-side bench-scale column evaluation comparing natural attenuation, bioventing, and biosparging using three soil cores collected in July 1997. Specific objectives of this study are to:

- a.* Determine potential microbial activity of Area 1795 subsurface soils.
- b.* Determine intrinsic total petroleum hydrocarbons (TPH) degradation potential of Area 1795 subsurface soils.
- c.* Determine parameters that will enhance subsurface microbial growth in Area 1795.
- d.* Optimize parameters using column study, which simulates natural subsurface conditions.
- e.* Generate data for design and preliminary cost evaluation for remediation of Area 1795.

Background

DETAILED MAPS CAN BE FOUND IN THE FIELD GUIDE, MAP SECTION OF THIS GUIDE.

FORT DRUM

★ ARMY COMMUNITY FACILITIES
See map of individual facilities and locations.

■ GATES TO PORT JEFFERSON

Area 1795 most recently contained two 94,600-ℓ (25,000-gal) and one 45,600-ℓ (12,000-gal) steel underground storage tanks (USTs) for unleaded gasoline and 10 dispenser pumps. The site was in use until the mid 1990s when the USTs, dispensers, and associated piping were removed. Fuel leaks from this storage and dispensing area has caused extensive contamination of soil and groundwater with petroleum hydrocarbons. The contamination includes free product at the groundwater surface and a dissolved phase plume that extends to a surface water stream located to the west of Area 1795. No documented estimates exist concerning the volume of petroleum products released to the environment from this site.

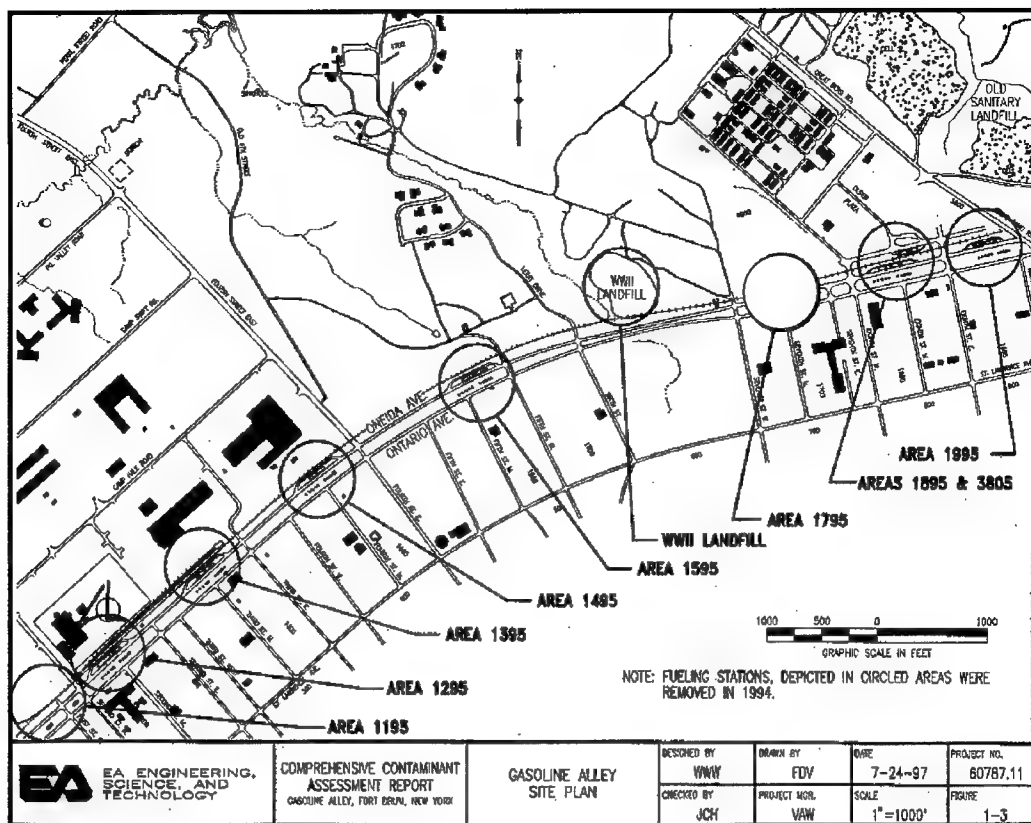


Figure 2. Gasoline Alley

A World War II (WWII) landfill is also located to the west of Area 1795. This landfill contains mounds of various surface debris materials. Debris in the landfill appears to be general refuse from Fort Drum and contain contaminated material which may be contributing to the contamination of soils and water in the area.

Characterization

Area 1795 and the contamination site are located on an unconsolidated sand aquifer. The aquifer consists of stratified layers of fine- to medium-grained sands extending to depths greater than 12 m (40 ft). Below the sand deposits are 0.9 to 1.5 m (3 to 5 ft) of silty sand, and approximately 0.6 to 1.5 m (2 to 5 ft) of very fine silt to clay. The unconsolidated aquifer is underlain by a limestone formation at a depth of 15 to 17 m (50 to 57 ft) below the ground surface.

Water table elevations fluctuate seasonally from 1 to 2 m (4 to 5.5 ft) in the area northwest of the contamination source but slightly less in the source area. Depth to the water table is approximately 3 m (10 ft) in the area. General groundwater flow in the area of concern appears to be toward the west-northwest from the source area and is intersected by a surface stream to the west of the contamination site. The mean hydraulic conductivity of the shallow aquifer in this area was estimated to be 64 m/day (211 ft/day) from well slug test. In 1996

the mean hydraulic conductivity was estimated to be 8 m/day (25 ft/day) based on a constant-rate aquifer pumping test. The average yearly subsurface temperature is 10 °C (50 °F).

Separate-phase product has been observed in 15 wells and piezometers located in the vicinity of the source area. The apparent thickness of separate-phase product ranged from a sheen to almost 0.9 m (3 ft) during 1995. Thickness of the separate-phase layer is reported to be the greatest during the fall of the year when the groundwater levels are at an annual low. Between July and December of 1996 during a pilot study of a separate-phase recovery system, 632 l (167 gal) of separate-phase product was removed from Area 1795 wells and piezometers. Data collected in 1995 suggest that the separate-phase plume covers an area of approximately 13,935 m² (150,000 ft²).

Vertical movement of the separate-phase contamination by seasonal groundwater fluctuations has created a "smear zone" of highly contaminated soil which has a thickness of approximately 0.9 m (3 ft). Based on estimates of the areal extent of the plume and the thickness of the smear zone, the volume of soil contained in the smear zone is estimated to be 12,743 m³ (450,000 ft³).

A petroleum contaminated groundwater plume extends approximately 549 m (1,800 ft) northwest of the former USTs location toward an unnamed creek to the west of Area 1795. Benzene, toluene, ethylbenzene, xylene (BTEX), and naphthalene were reported at the greatest frequency in the groundwater. The nature of contamination in the groundwater suggests that gasoline is the primary product contributing to groundwater contamination. Surface water and sediment data from the creek indicate that the creek may be affected by the groundwater plume.

Collection of Soil Cores and Groundwater

Soil

Soil cores were extracted from Area 1795 on two occasions. In March 1997, one core was extracted near well MWS6 and used for chemical and biological characterization of the subsurface and for microbiological assays. This information is the focus of the Phase I report. In July 1997, three additional cores were extracted for use in the bench-scale column treatability study described in this report. Each of these cores was extracted within a 3-m (10-ft) radius of the original core extracted in March 1997. The site for core extraction was determined jointly by the USAED, Baltimore, and EA Engineering personnel based on results from the contaminant assessment report for Area 1795 and site worker knowledge of recent sampling events.

Soil cores were extracted using a drill rig with a split-spoon sampler (Figure 3). These cores spanned a continuous depth to approximately 5 m (15 ft) below the ground surface reaching several meters (feet) below the groundwater table. Site personnel indicated that the groundwater table was at a depth of 4 m (12 ft) at the location and time of core extractions. Soil was collected in acetate liners approximately 1.5 m (5 ft) in length located inside the split-spoon sampler. Each acetate liner was capped and sealed with a paraffin wax when brought to the (Figure 4). Cores were placed in a refrigerated trailer at 4 °C and shipped to ERDC.

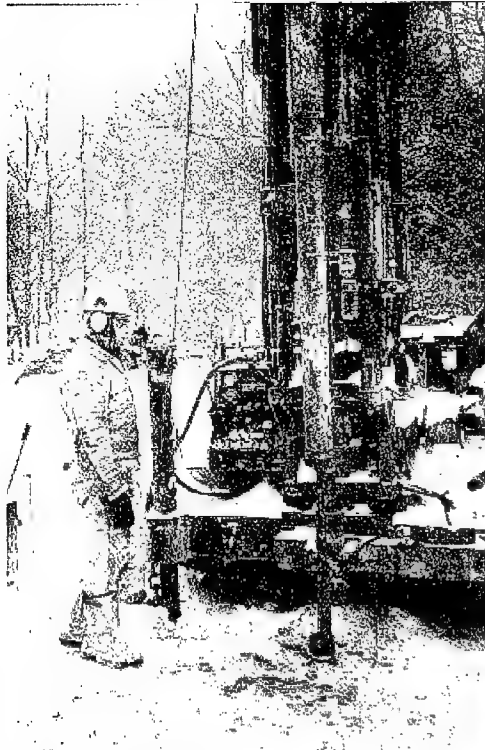


Figure 3. Drilling rig

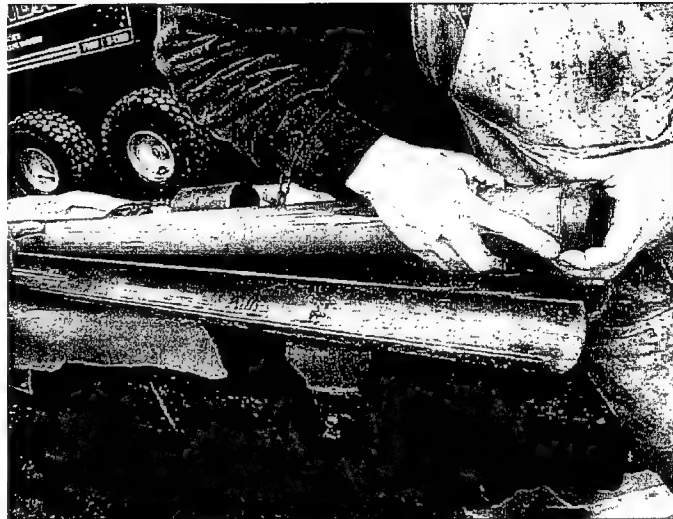


Figure 4. Soil core in acetate liner

Groundwater

Groundwater samples were extracted in March 1997 in conjunction with initial subsurface cores sampling activities. Groundwater was collected from well 1795-MWS6 (Figure 5) and stored in 189.25-l (50-gal) containers at 4 °C until used in one of the treatability studies.

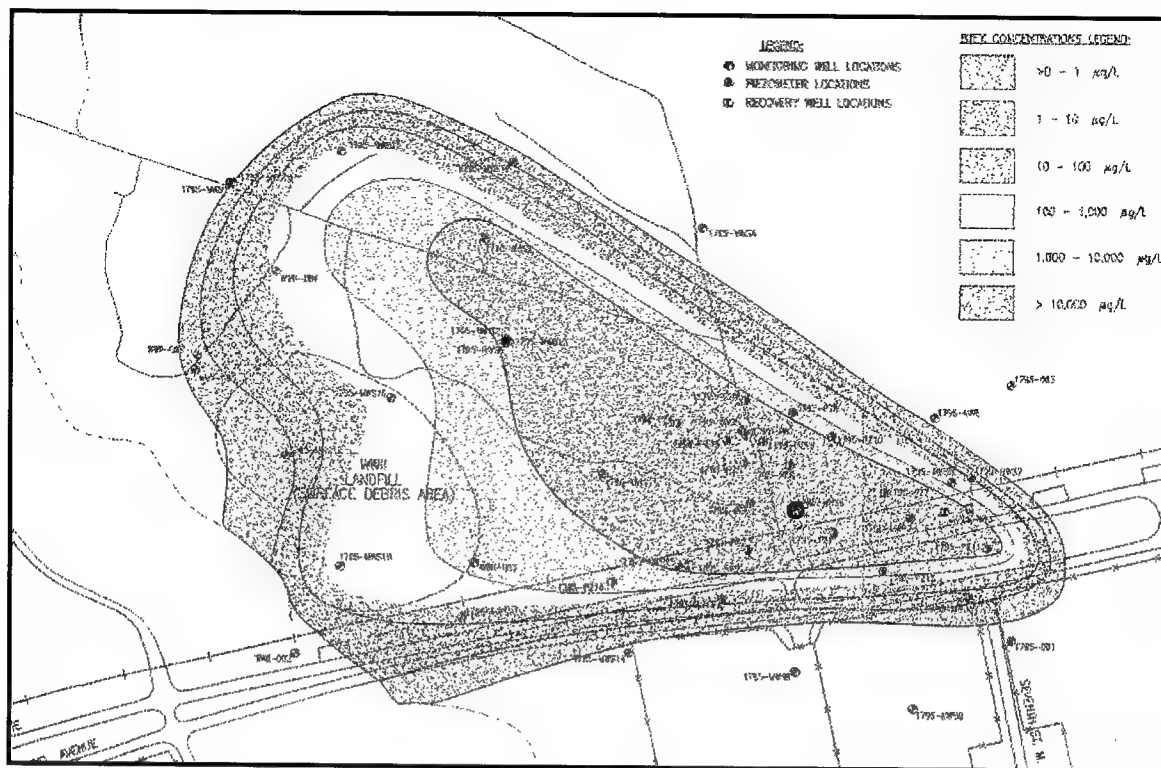


Figure 5. Location of well 1795-MWS6 (circled in red) for groundwater and soil cores

2 Phase I–Microcosm-Scale Evaluation

Background

Respirometry flask studies can be used to: (a) evaluate potential for microbial activity, (b) evaluate potential for degradation of contaminant of concern by native consortia, (c) screen available treatment options, and (d) refine the objectives of larger-scale treatability studies. The screening work at the microcosm scale (< 250 ml) provides data necessary for making informed decisions prior to initiating larger-scale, more expensive evaluations. In addition, the small scale of microcosm studies allows replication necessary to conduct statistical analysis.

Objectives of Phase I

The primary objectives of this phase of the study were to:

- a.* Develop a vertical profile of TPH contamination.
- b.* Determine the vertical distribution of viable microorganisms.
- c.* Determine basal microbial activity of native consortia in subsurface soils.
- d.* Determine the intrinsic potential of native consortia to degrade TPH.
- e.* Determine parameters that will enhance degradation of TPH in the subsurface.

Experimental Approach

A continuous vertical subsurface soil core extracted from Area 1595 in March 1997 was chemically characterized for contaminant concentration and biologically characterized for microbial biomass and community structure. Soil samples were removed from the core. Cell membrane lipids, phospholipid fatty acids (PLFA) and TPH, were removed from the soil samples by solvent

extraction. Extracts were analyzed by gas chromatography and mass spectrometry. The resulting chemical and biological profiles were compared so that discernable relationships between contaminant distribution and microbial community could be determined.

The basal microbial metabolic activity potential of subsurface indigenous microorganisms was determined by radio-respirometry assays using ^{14}C -labeled acetate. Acetate was chosen for this challenge because it can be easily utilized by most microorganisms as a source of energy and/or carbon. Mineralization of acetate was considered unequivocal evidence of microbial respiration.

Phenanthrene was chosen as a challenge to determine the potential of native microorganisms to degrade TPH. Phenanthrene has a low volatility relative to other fuel range hydrocarbons resulting in greater analytical recovery. Phenanthrene is also relatively recalcitrant when compared with other fuel range hydrocarbons, and therefore degradation results will represent conservative estimates of overall microbial activity on bulk hydrocarbon contamination.

The intrinsic ability of soil microflora to mineralize petroleum hydrocarbons was established in two ways. Mineralization of ^{14}C -labeled phenanthrene in radio-respirometry assays established microbial respiration using phenanthrene. Comparison of initial and final concentrations of contaminant in respirometry flasks established overall contaminant degradation during the experiment.

Methods and Materials

TPH and PLFA analytical methods for soil

TPH and PLFA in the soil sample were recovered by extracting 1 g of soil in 3.5 ml of an organic solvent solution consisting of methylene chloride, methanol, and aqueous phosphate buffer in the proportions 5:10:4 on a volumetric basis. The soil solvent mixture was sonicated for 2 min and allowed to equilibrate for a period of 3 hr at room temperature. Following the extraction, 1 ml methylene chloride and 1 ml water were added to the solution. This resulted in a two-phase separation consisting of a nonpolar phase containing organic lipids and an aqueous phase. The nonpolar phase was recovered and passed through a prepacked silica-gel column containing 0.5 g of silica gel. To further separate the nonpolar materials, the column was then washed sequentially with 5-ml methylene chloride (extracting petroleum hydrocarbons), 5-ml acetone, and 5-ml methanol (extracting lipids). Each eluted solvent was collected separately for analysis.

TPH quantification was performed by injecting 1 μl of the methylene chloride recovered from the silica gel column on an HP-6890 gas chromatograph (GC) equipped with an SPB-5 capillary column (60m, 0.32mm ID, 0.25 μm film). The column temperature program was as follows: 50 $^{\circ}\text{C}$ for 2 min, increased to 310 $^{\circ}\text{C}$ at a constant rate of 4 $^{\circ}\text{C}$ per minute, and then held at 310 $^{\circ}\text{C}$ for 3 min. A 1-min splitless injection was used at a purge of 80 ml/min. The injector was maintained at 250 $^{\circ}\text{C}$ and the flame ionization detector at 320 $^{\circ}\text{C}$. Nonadecanoic acid methyl ester at 50 pmole/ μl was used as an internal standard. An internal standard calculation was used to convert total peak area between retention times

of 10 and 50 min into TPH concentration. Reproducibility of the gas chromatographic analyses averaged a standard error of 9 percent while replicate analyses of soil extracts (1-g size) averaged a standard error of 15 percent for the soil column soils. The range of error was much greater for the soil analyses where a minimum error of 5 percent and a maximum error of 39 percent were seen. In both phases of this evaluation, an estimated standard deviation of 20 percent was assumed for all soil sampling points where only one sample was taken.

TPH. TPH recovery from the soils in this experiment, by the method described above, was 58 ± 5 percent. Soil TPH values reported in this study are for the recoverable TPH (rTPH). rTPH values are not corrected to include that fraction of the rTPH in the soil which is not recoverable. Recovery of TPH from a clay reference soil, by the method described above, was approximately 85 percent, which is a more typical value. An independent analysis of soil samples was performed by Argus Analytical, Inc., Jackson, MS. Recovery percentages and rTPH concentrations determined by Argus Analytical, using Environmental Protection Agency (EPA) Method 3550 for soil extraction and EPA Method 8015¹ for analysis, correlated well with the results obtained by the method described above (Table 1). Because recovery of petroleum hydrocarbons from a sandy soil are usually high, the low recovery from the sandy Fort Drum soils suggests that something other than a normal sorption process of the petroleum hydrocarbons to the soil particles is affecting the recovery of TPH.

Table 1				
rTPH Analytical Method Comparison				
Sample Location	Depth m bgs ft bgs	rTPH (mg/kg)		
		WES Bligh-Dyer Extraction, mg/kg	WES EPA Method (s.d.)	Argus Labs, Inc. EPA Method, mg/kg
1595	3.2 (10.5)	507	483 (73)	158
	3.5 (11.5)	13,369		13,700
1795	9.5	50		36
	12.0	1,924	4,750 (789)	154
3805	22.0	17		35
	32.0	14	4 (4)	0
Notes: bgs denotes below ground surface; s.d. denotes standard deviation.				

PLFA. The methanol fraction recovered from the silica-gel column was dried under nitrogen and then subjected to trans-esterification in mildly alkaline methanol to form methyl esters of the ester-linked PLFA. PLFA were identified and quantified on a HP-5973 mass selective detector interfaced to an HP-6890 GC. The GC was equipped with a J&W DB-5ms capillary column. During each injection, the column temperature was held at 80 °C for 2 min, increased to 150 °C at a constant rate of 10 °C per min, then increased to 282 °C at 3 °C per

¹ U.S. Environmental Protection Agency. (1992). "Test methods for evaluation of solid waste and emergency response," SW-846, Office of Solid Waste and Emergency Response, Washington, DC.

min, and held at 282 °C for another 2 min. A 2-min splitless injection of 1 µl at a purge of 80 ml/min was used. The injector was maintained at 270 °C. Mass spectra were collected at 70 electron volt (ev) using positive electron impact.

Microcosm flask setup

Respirometry flasks (250-ml) from Reliance Glass were used for the microcosm studies (Figure 6). Flasks were acid washed, dried, and rinsed with 5 to 10 ml dichloromethane and air dried in a Biofree clean hood. Flasks, caps, and hydroxide wells were sealed with aluminum foil and double autoclaved. Aliquots of soil were placed into the flask and challenged with radio labeled tracer compound. Flasks were equipped with center wells that contained 2 ml of a 1N potassium hydroxide solution. $^{14}\text{CO}_2$ resulting from mineralization of ^{14}C -labeled acetate or ^{14}C -labeled phenanthrene was trapped as carbonate in the hydroxide solution. The hydroxide solution was removed from the well using a syringe or a pipette at regular intervals (based on rate of microbial respiration) for analysis by a Hewlett Packard liquid scintillation counter (LSC). Fresh hydroxide solution was placed in the well immediately after withdrawing the used hydroxide solution.

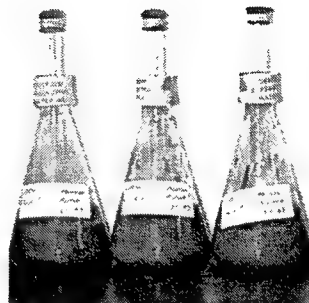


Figure 6. Example respirometry flask

Results and Discussion

Data developed from Phase I is provided in Appendix A.

Vertical distributions of rTPH and microbial characterization

The distributions of rTPH and microbial biomass (PLFA estimates) along the depth of the soil core are presented in Figure 7. Measurable TPH contamination in the Area 1795 soil core was limited to the bottom of the core, 4 m (12 ft) below the ground surface. The rTPH concentration at this level was approximately 1,000 ppm ($\mu\text{g/g}$ of wet soil). The contamination in the Area 1795 soil core was both at lower levels and less distributed than that found in the Area 1595 soil core.

A conversion of membrane lipid content to cell numbers showed the soil to contain approximately 7×10^8 cells g^{-1} (wet weight) at the ground surface, which is a typical value for ground surface biomass levels. This cell density is comparable to that observed at Area 1595 ($\sim 4 \times 10^8$ cells g^{-1}). Typical subsurface biomass profiles show an order of magnitude decrease within the first 0.3 to 1.5 m (1 to 5 ft) followed by another order of magnitude decrease by the 3- to 15-m (10- to 50-ft) depth.

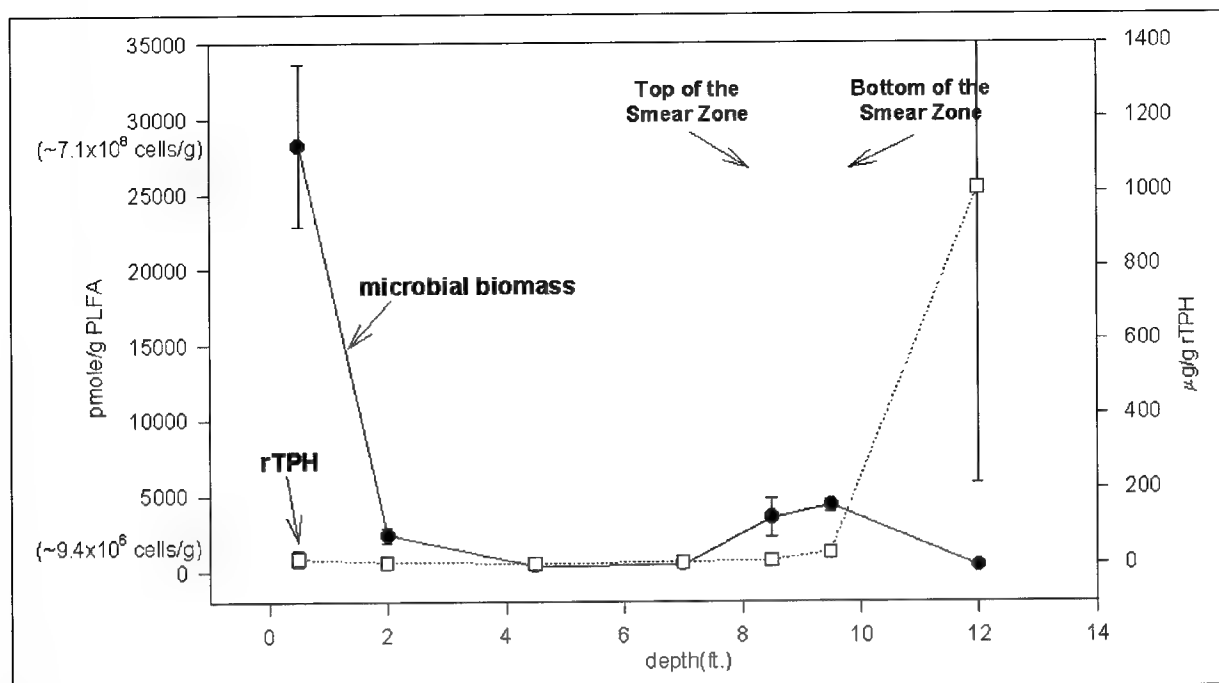


Figure 7. Vertical biomass and contaminant profile

The surface biomass decreased two orders of magnitude to a value of $\sim 9.4 \times 10^6$ cells g^{-1} by a depth of 0.6 m (2 ft). This same pattern was also observed at Area 1595, although the magnitude of the decrease was less at Area 1595. There was a significant increase in subsurface microbial biomass at the 2- to 3-m (8- to 10-ft) depth of the soil column. This increase occurred near the top of the zone of rTPH contamination in the core. This increase of subsurface biomass in close proximity to the rTPH-contamination zone suggests a contaminant influence on microbial growth (as was observed at Area 1595).

Microbial community

In addition to determining microbial abundance, microbial community composition can be estimated from the examination of lipid biomarkers. Phospholipids are the building blocks of life and, as such, all living organisms contain them. Bacteria contain a unique subset of phospholipids allowing for their identification in environmental samples. In addition, the structure of phospholipids (which comprise the bulk of a bacterial cell membrane) can be used to taxonomically identify bacterial genera. Figure 8 illustrates how microbial community composition (based on lipid biomarkers, i.e., phospholipids) varied with depth and contaminant concentration.

Redox potentials, and associated microbial induced reactions, often follow a pattern whereby oxidation of carbon is followed by the reduction of molecular O_2 , the reduction of nitrate, the reduction of ferric hydroxide, and the reduction of sulfate. This pattern is typically seen from outside to inside of a contamination plume. The selection of the above microbial classifications can be related to this pattern. For example, both Gram-positive and Gram-negative bacteria can accomplish oxidative metabolism. There are a number of

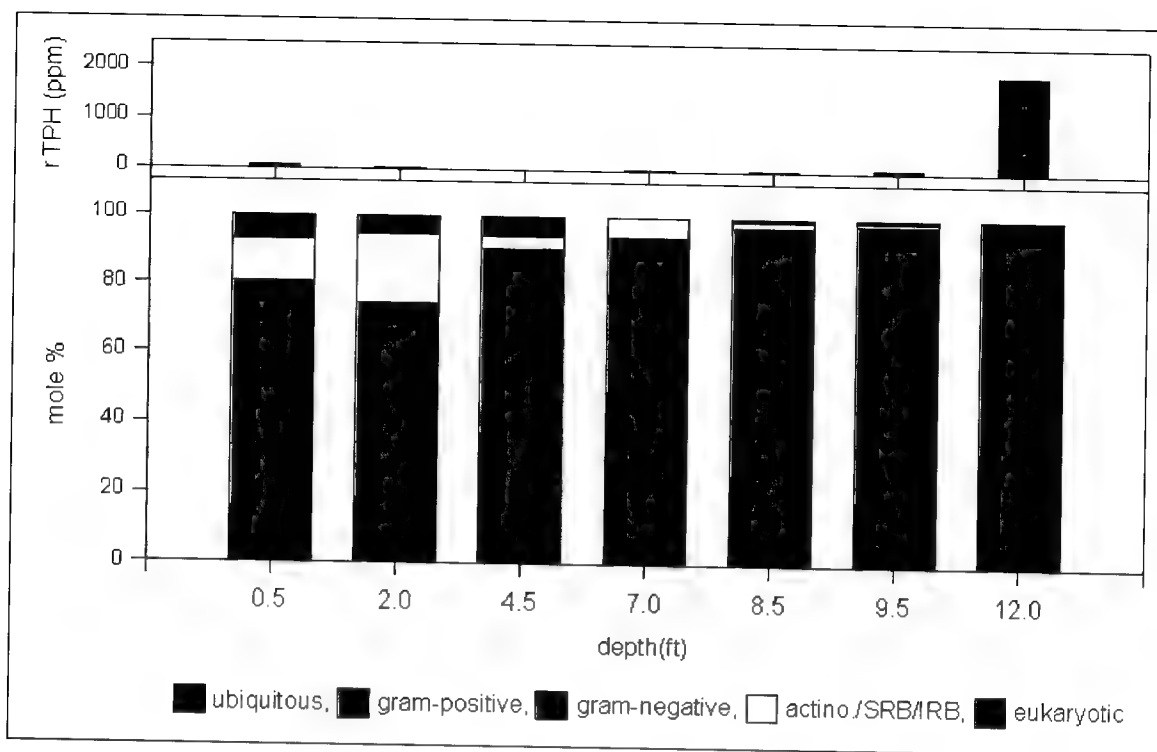


Figure 8. Vertical microbial community and contaminant profile

differences between Gram-positive and Gram-negative bacteria, but from an ecological point of view, two differences stand out. Gram-positive bacteria have relatively complex nutritional requirements and are resistant to physical disruption whereas Gram-negative bacteria have relatively simple nutritional requirements and are less resistant to physical disruption. Actinomycete, sulfate reducing bacteria, and iron-reducing bacteria (Actino./SRB/IRB) are even more specialized classifications of bacteria and as the names imply, are capable of the reductive metabolism of certain substrates. Micro-eukaryotes, such as fungi, protozoa and micro-algae, are also found in certain subsurface environments. Certain fungi have been identified to possess the capacity to mineralize contaminant substrates (ex. *Penicillium* and *Cunninghamella* have degraded petroleum hydrocarbons).

Based on a comparison of lipid profiles by using a similarity measure (hierarchical cluster analysis, data not shown), the community composition of the extant subsurface microbiota in Area 1795 was similar to that observed in Area 1595 soils. Analysis of the microbiota in Area 1795 soils revealed a trend toward increased ubiquitous lipid biomarkers (nondescriptive taxonomically) and decreased micro-eukaryotic lipid biomarkers to a depth of approximately 2 m (7 ft). This trend was then reversed between the depths of 2 and 4 m (7 and 12 ft). The lower half of the core also showed an increasingly (with depth) greater percentage of Gram-negative bacterial lipid biomarkers. The increase in the ubiquitous lipid markers, although not diagnostic with respect to taxonomy, can be related to changes in the physiological status of the extant microbiota. Typically, an increase in the percentage of the lipid biomarkers comprising this

classification, is associated with a decrease in cell membrane fluidity. This change in membrane fluidity can be directly related to changes in the external environment (ex- pH, carbon, nutrients, or xenobiotic) most of which were not measured in this study. The community described at the bottom of the core (4-m (12-ft) depth) where rTPH concentrations increase is similar in composition to that observed in Area 1595 where evidence of insitu biodegradation of petroleum hydrocarbons was identified. The increased relative percentage of Gram-negative bacterial lipid biomarkers (in the lower half of the core) is also conducive to the occurrence of insitu hydrocarbon biodegradation. Correlation analysis identified significant relationships between Gram-negative bacterial relative abundance and rTPH concentrations in Area 1795 and Area 1595 soils (Table 2). The *Pseudomonas* sp. of bacteria is classified as Gram-negative and has been identified in the successful biodegradation of petroleum hydrocarbons. A number of other Gram-negative bacterial genera have also been demonstrated to have the capacity to mineralize petroleum hydrocarbons. The community described at the bottom of the Area 1795 soil core is consistent with the presence of such organisms. In addition, the eukaryotic presence identified at the bottom of the core is attributable to fungi (based on the presence of specific lipid biomarkers).

Table 2
Significant ($p > 0.05$) Correlations (r^2) between Gram-Negative Bacterial Lipid Biomarkers (PLFA) and rTPH Concentration

Lipid Biomarkers	Area 1595	Area 1795
General Gram-negative	0.77	0.89
<i>Pseudomonas</i> sp.	0.87	0.79
Other sp.	0.96	0.82

Acetate challenge respirometry

After validating the existence of potentially viable microorganisms in the subsurface of Area 1795, a series of respirometry flask evaluations were conducted to establish the catabolic potential of the existing microorganisms. Table 3 shows the experimental design for the C^{14} -acetate challenge.

Table 3
Experimental Design for Tracer Acetate Challenge

Upper Smear Zone		Lower Smear Zone	
Saturated	Unsaturated	Saturated	Unsaturated
X	X	X	X

Note: All evaluations conducted in triplicate.

Results displayed in Figure 9 indicate that activities of the indigenous microbial populations at Area 1795 were low. Challenge assays with the readily utilizable substrate acetate resulted in only 5 percent cumulative mineralization over a 200-hr incubation period. This level of mineralization was only obtained under unsaturated conditions in soil collected from the bottom of the smear zone. Microbial populations in soils collected from the top and bottom of the smear zone and maintained under saturated conditions did not mineralize the added substrate to an appreciable level. These activities are considerably lower than those observed in Area 1595 soils, as were the measures of total microbial biomass.

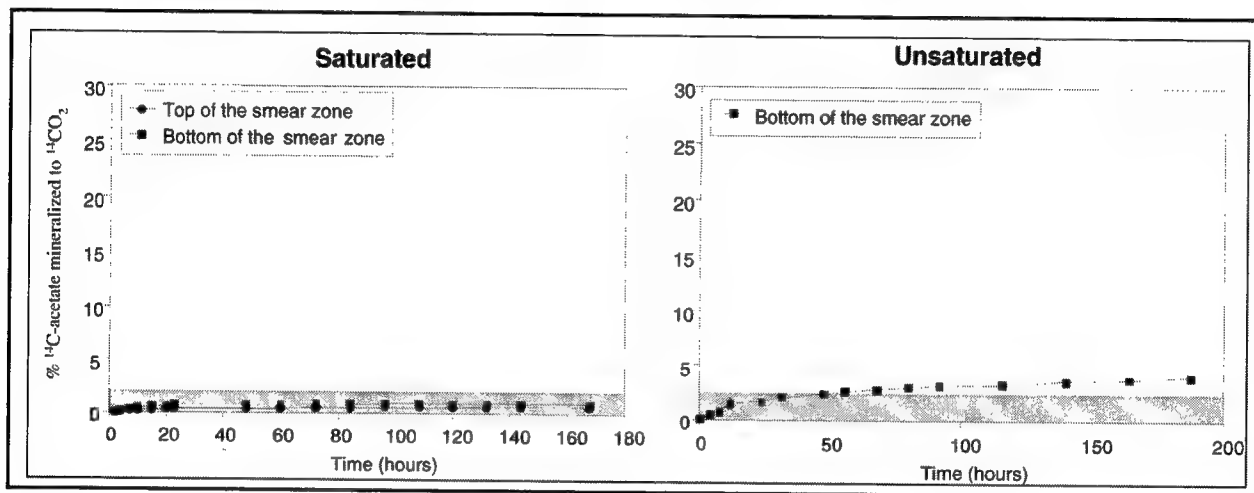


Figure 9. Respirometry results from acetate challenge

Phenanthrene challenge respirometry

Experimental treatments chosen for the phenanthrene challenge (Table 4) were selected to simulate plausible full-scale insitu remediation strategies including the addition of hydrogen peroxide and the addition of nutrient amendments. Hydrogen peroxide was chosen as a method of oxygen delivery because of its ability to maintain desirable oxygen concentrations in groundwater further from the source well than sparging with air or oxygen. Hydrogen peroxide was added to the flask at a concentration of 4.76 mg per gram of soil. This concentration was demonstrated to be beneficial to aerobic microorganisms in previous studies at WES. Nutrient solution, MiracleGro[®], was added at a concentration of 8.4 mg per gram of soil. MiracleGro[®] used in this study contained 7 percent total nitrogen (0.4 percent ammoniacal and 6.6 percent urea), 7 percent available phosphate (P₂O₅), and 7 percent soluble potash by weight. The added concentration of each nutrient to flasks was therefore 0.59 mg per gram of soil.

Recovery data, ¹⁴C-CO₂, of the phenanthrene challenge are shown in Figure 10. In contrast to results from the acetate challenges, challenges with phenanthrene did result in significant mineralization. Microbial population in soils from the top and bottom of the smear zone mineralized the added contaminant under saturated conditions, but only the biota associated with soils from the top of the smear zone were capable of mineralizing the contaminant under unsaturated conditions. Amendments in the form of H₂O₂ and nutrients did

Table 4
Experimental Design for Phenanthrene Challenge

	Upper Smear Zone		Lower Smear Zone	
	Saturated	Unsaturated	Saturated	Unsaturated
Sterile Control	X	X	X	X
Control (Head Space Air)	X	X	X	X
Nutrient (NPK – 7:7:7)	X	X	X	X
H ₂ O ₂	X	X	X	X
H ₂ O ₂ + Nutrient	X	X	X	X

Note: All evaluations conducted in triplicate.

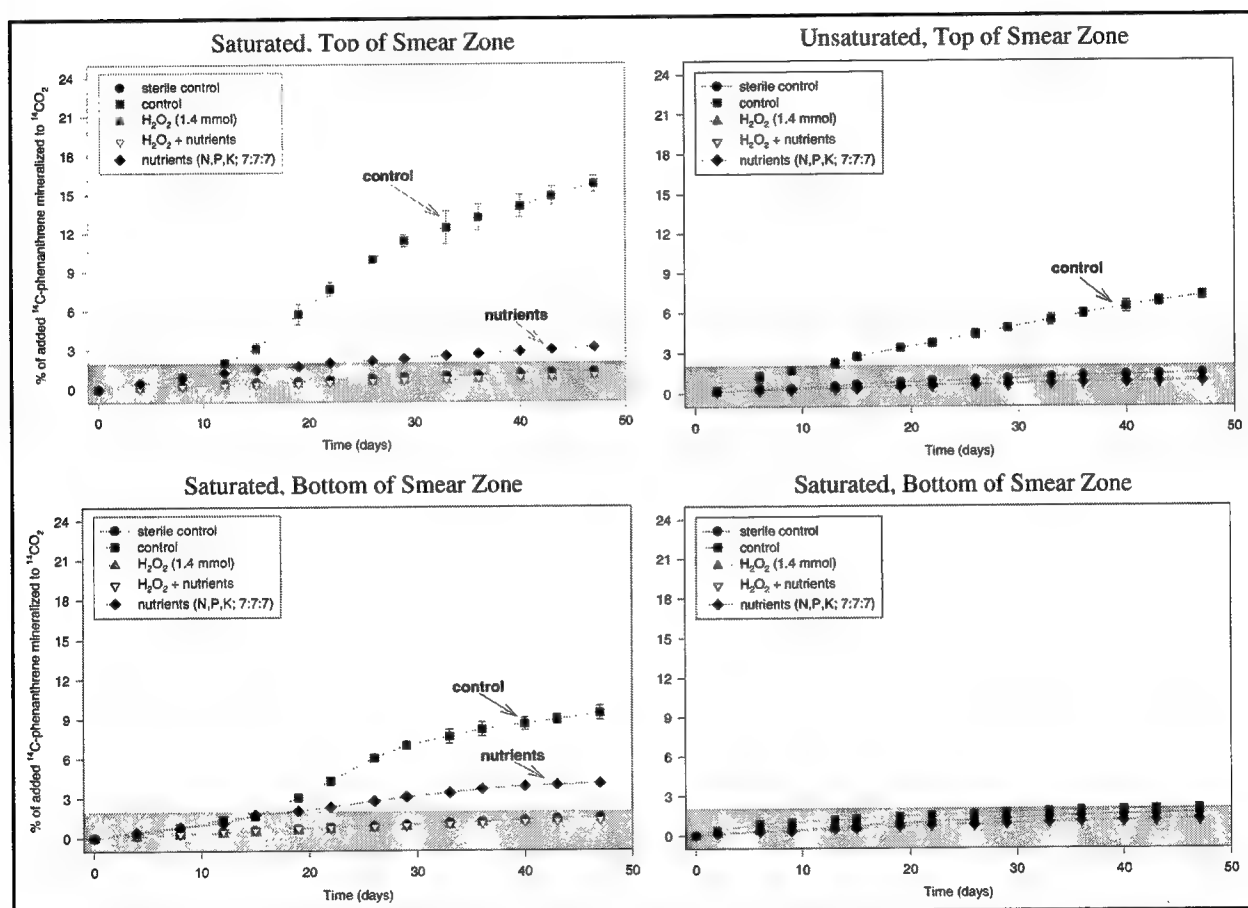


Figure 10. Respirometry results from phenanthrene challenge

not enhance mineralization levels above those measured for the unamended control. These results are comparable to those obtained from Area 1595 soils. Although, the levels of general microbial activity were quite low in the Area 1795 soils, significant levels of contaminant mineralization were observed under both saturated and unsaturated conditions.

The lack of acetate mineralization is atypical of what is usually observed in subsurface environments. The isotope mass balance for Area 1795 acetate microcosm showed a greater than 90 percent recovery of the added label and a 74 to 92 percent partitioning into the aqueous phase (data not shown). This pattern is typical of a sterile environment (acetate is soluble in water). However, significant mineralization of added phenanthrene was observed (Figure 10). Based on the data collected, it can be speculated that a highly specialized community of microorganisms existed in these soils (i.e., selection for the capacity to metabolize polynuclear aromatics) or that the extant biota existed in a state of dormancy, requiring a period of time for adjustment before metabolism occurred.

Conclusions from Phase I

Although the presence of viable microorganism is essential to any successful bioremediation effort, biomass must also have the capacity to actively metabolize the contaminant. An initial screen was performed on soils recovered from the subsurface core collected from Area 1795. The screen showed only slightly elevated levels of biomass in the subsurface. Only the microbiota in soil recovered from the 3-m (9.5-ft) depth and incubated under unsaturated conditions showed any significant mineralization (5 percent) of ^{14}C -acetate in the 8-day study. In longer-term incubation studies, microorganisms from the soil samples taken at the 2.6- and 2.9-m (8.5- and 9.5-ft) depths showed significant mineralization of phenanthrene under saturated conditions utilizing only the oxygen from the air in the flask headspace. This information suggests that the microorganisms are capable of mineralizing rTPH. This information also suggests that because of low microbial populations in the subsurface, there may be considerable lag phase (1 month or longer) before significant microbial activity takes place. In addition, microbial community structure in Area 1795 soils showed a close similarity to those of Area 1595, an area where in situ biodegradation of the rTPH contamination was identified.

Experimental results from Phase I indicate biological remediation of subsurface contamination at Area 1795 is a viable alternative based on the following:

- a. A viable microbial biomass was detected in the area of subsurface rTPH contamination.
- b. Endogenous microbial populations demonstrated the ability to mineralize phenanthrene during a 47-day radiotracer challenge evaluation.

- c.* Specific microbial community biomarkers correlated significantly with rTPH concentration indicating a direct response (of the extant microbiota) to the contamination.
- d.* Addition of amendments, other than molecular oxygen from the flask headspace, did not show an improvement in rTPH (as phenanthrene) degradation.

3 Phase II–Bench-Scale Column Studies

Objectives

The objective of this study was to provide site-specific information to HTRW - USAED, Baltimore, and Fort Drum Environmental Public Works, relevant to alternative remediation technologies, to assist in making informed engineering decisions for follow-on remediation activities. To meet this objective, bench-scale column studies were conducted using three soil cores from Area 1795 of Gasoline Alley. These column studies were used to produce a side-by-side evaluation of bioventing, biosparging, and natural attenuation treatment alternatives for Area 1795. Because the addition of hydrogen peroxide showed no enhancement of biological degradation of phenanthrene in Phase I of this study, sparging of air in the saturated zone (biosparging) was investigated as a method of oxygen delivery instead of hydrogen peroxide addition.

Experimental Design

The bench-scale soil-columns study was designed to simulate the insitu conditions of the contamination site. To accomplish this, soil columns were kept in a walk-in cooler that was dedicated to this study for the duration of the experiment. The cooler temperature during the study was maintained at 10 °C, the average yearly subsurface temperature for the Fort Drum area suggested by Mr. James Spratt, USAED, Baltimore.

Soil-core material was packed in custom-manufactured glass columns with an inside diameter of 8 cm (3.25 in.) and a height of 1.8 m (6 ft). Acetate liners were cut into approximately 46-cm (18-in.) sections and the soil was forced out of these sections into the top of the columns. Soil from the liners was added, beginning with the bottom of the core and ending with the top. This packing technique did cause local mixing of the soil but maintained the vertical profile of the soil core. To accommodate the 5-m (15-ft) depth of the cores, two columns were connected in series with 6.4-mm (¼-in.) stainless steel tubing for each core. Sample ports were located at approximately 0.3-m (1-ft) intervals along the

length of the column. The inside diameter of the glass columns was larger than that of the acetate liner, which resulted in a reduction of total height between the soil core and the glass column. A listing of column ports, their depth from the top of soil column, and correspondence with core depth below ground surface is presented in Table 5.

Table 5		
Column Depth vs Core Depth		
Column - Port	Column Depth, cm (In.)	Core Depth, cm (In.)
2-Top	0 (0)	0 (0)
2-58	7 (2.8)	10 (3.9)
2-46	19 (7.5)	26 (10.2)
2-34	31 (12.2)	43 (16.9)
2-23	42 (16.5)	58 (22.8)
2-10	55 (21.7)	76 (29.9)
2-0 & 1-Top	65 (25.6)	90 (35.4)
1-58	72 (28.3)	99 (39.0)
1-46	84 (33.1)	116 (45.7)
1-34	99 (39.0)	137 (53.9)
1-23	107 (42.1)	148 (58.3)
1-10	120 (47.2)	166 (65.4)
1-0	130 (51.2)	179 (70.2)

Note: To obtain centimeters, multiply inches by 2.54.

Each port was closed with a 25-mm Teflon plug. Plugs used in ports 1-10 and 1-23 were drilled, tapped, fit with two-way valves, and packed with glass fiber. These ports were used for taking water samples. The plug used in port 1-34 of the bioventing column was fit with a tubing connector for connection to airflow tubing. The ends of each column were closed with a 50-mm Teflon plug that was screened with a 50-mm diffuser stone. Each end cap was tapped and fit with a tubing connector.

A schematic of the columns for bioventing and biosparging is shown in Figure 11. Figures 12 and 13 show the actual Area 1795 column setup.

To simulate the saturated zone of the contamination site, groundwater from the site was added through port 1-0 at the bottom of the first column to a height of approximately 81 cm (32 in.).

Forcing breathing-grade air from a pressurized cylinder through specified ports in the respective columns simulated bioventing and biosparging. For biosparging, the air was forced in port 1-0 located in the column end cap. This location was at the bottom of the simulated saturated zone. For bioventing, the air was forced into the center of the column through stainless steel tubing placed through port 1-34. This location was in the smear zone and was approximately 5 cm (2 in.) above the simulated saturated zone. An on-off valve, mass-flow meter, and check-valve in series controlled the flow of pressurized air into each

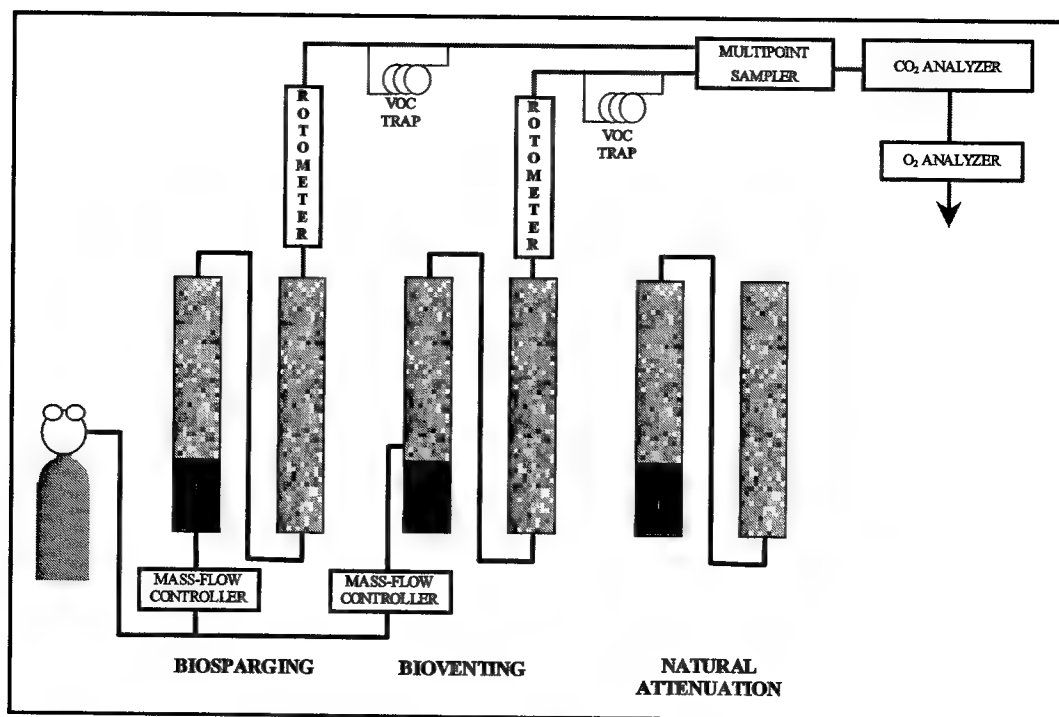


Figure 11. Column design (VOC = volatile organic carbons)

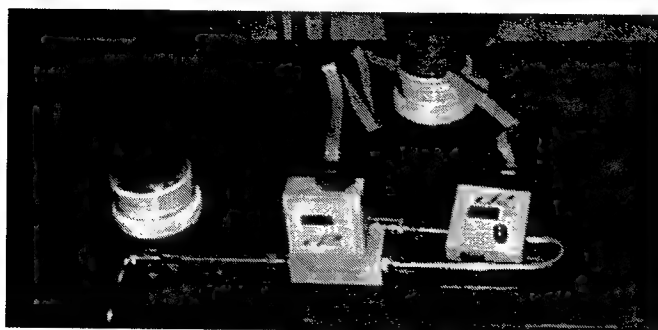


Figure 12. Flow control

series of columns. All the ports in the bioventing and biosparging columns were tested and ensured for absence of air leaks.

The desired airflow rate (1 standard cubic centimeter per minute, sccm) was calculated

using the guidance given in the EPA Manual – Principles and Practice of Bioventing – Volume II: Bioventing Design.¹ A higher flow rate (4sccm) was also used in both the biosparging and the bioventing columns to determine the effect of airflow rate in excess of the EPA recommendations. Because the airflow rates recommended by the EPA manual for bioventing are calculated on the basis of soil volume treated, the same airflow rate was used in both bioventing and biosparging columns to give an unbiased comparison between the two treatment methods. Airflow was delivered in a continuous stream to the columns except during sampling periods at which time the airflow was halted. Airflow through the columns was initiated at 4 sccm, approximately four times the rate calculated using the EPA recommendations, and maintained at this rate

¹ U.S. Environmental Protection Agency. (1995). "Principles and practice of bioventing–Volume II: Bioventing design," Washington, DC.



Figure 13. Columns

for 16 days. During the 42 days of the study, the airflow was reduced to the calculated EPA recommendation of 1 sccm.

No air was forced into columns simulating natural attenuation in the aquifer.

Methods and Materials

Sampling and analysis of off-gases

Air forced through the columns was collected at the exit in Tedlar™ bags and analyzed for oxygen and carbon dioxide concentrations. Air collected in the Tedlar bags was periodically drawn from the bags by a multipoint sampler and passed sequentially through a photoacoustic infrared multigas analyzer, a fuel-cell-type oxygen detector, and then exhausted. The multigas analyzer was used for measurement of CO₂ concentration in the exit air. The multigas analyzer had a minimum CO₂

detection limit of 13 ppm (by volume), a detection span of five orders of magnitude, and a resolution of 0.01 ppm. The accuracy of the instrument in the calibration range for this study was ± 10 ppm. The multigas analyzer also measured and compensated for the effect of water vapor in the air. The oxygen analyzer measured oxygen concentration from 0.01 to 100 percent (by volume) with a resolution of 0.01 percent and an accuracy of ± 0.01 percent. The Tedlar bags were emptied after the completion of each sample period and reused. The exit gas carbon dioxide data were logged automatically into a computer, shown in Figure 14. Oxygen and carbon dioxide analyses could not be performed for the natural attenuation columns, since no air was forced through these columns.

Analysis of VOCs in the off-gases from the column was attempted. Air exiting from the biosparging and bioventing columns was passed through TENAX traps for a known amount of time. These traps were then extracted, and the extract analyzed by gas chromatography for VOCs. Because there was no airflow through the natural attenuation columns, a VOCARB trap was connected to the headspace at the top of the soil column for a known amount of time, approximately 2 weeks. The VOCARB trap was then analyzed by gas

chromatography. However, analysis of the data indicated that the traps were being saturated, and therefore reliable volatilization rates could not be calculated.

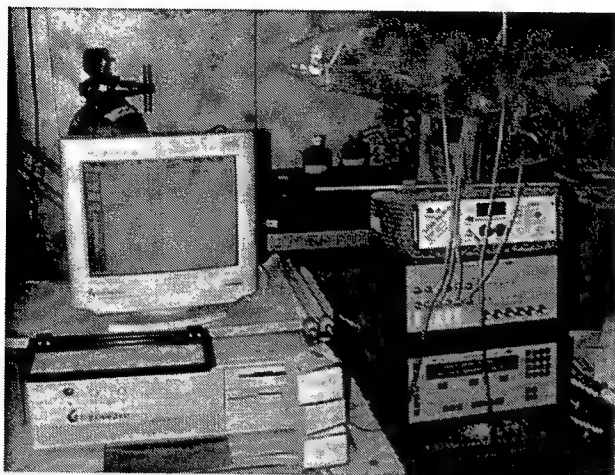


Figure 14. CO₂ and O₂ analytical equipment

Soil and water sampling

Soil and water samples were taken from the columns at specified times. A schedule of sampling is presented in Table 6. Airflow into the bioventing and biosparging columns was stopped approximately 2 hr before each sample period. After water and soil sampling was complete, contaminated water from Area 1795 was

added to each column through port 1-0 to return the water level to a height of 81 cm (32 in.) from the bottom of the column. Each sampling event lasted 8 to 12 hr. After each sampling event, airflow in the column was resumed.

Water sampling method. Water samples were taken from ports 1-23, 1-10, and 1-0 for each set of columns. All the free water was drawn from port 1-23, followed by port 1-10, then port 1-0. By taking samples in this manner, samples from port 1-23 represented the top of the saturated zone, samples from port 1-10 represented the middle of the saturated zone, and samples from port 1-0 represented the bottom of the saturated zone.

Samples were drawn from the ports by connecting a length of Tygon™ tubing to the valve attached to each of these ports. The valve was opened and the water was drawn through the tubing by an occlusion-type pump directly into sample vials. For each sample port, two 40-ml vials of pore water were collected first, followed by the collection of all remaining water into 125-ml sample bottles. The 40-ml sample vials were collected for the purpose of VOC analysis. Hydrochloric acid (HCl) (0.2 ml, 65 to 80 percent) was added to each vial to preserve the samples. The sample vials were filled completely to eliminate headspace when sealed. Samples were stored at 4 °C until their delivery for analysis the following day. The water collected in 125-ml sample bottles was used for analysis of polycyclic aromatic hydrocarbons (PAHs). These samples were also stored at 4 °C until delivered for analysis the next day.

Soil Sampling Method. Soil samples were collected after taking water samples. Soil samples were also taken following the sample schedule shown in Table 6. Only the initial and final soil samples were taken from the bottom of each column, ports 1-0 and 2-0, because of the difficulty involved in sampling this location. Soil samples from the top of each column, ports 1-Top and 2-Top, were taken only during the first, third, and last sample periods for the same reason. Soil samples collected during the initial and final sample period were

Table 6
Sampling Schedule

		Date	8/29/97	9/1/97	9/3/97	9/18/97	10/2/97	10/14/97	10/30/97
		Days Since Start	0	3	5	20	34	46	62
		Days Between Samples	0	3	2	15	14	12	16
		Airflow Between Samples (scm)	0	0	4	4	1	1	1
Column-Port	2-TOP	S			S				S
	2-58	S			S	S	S	S	S
	2-46	S			S	S	S	S	S
	2-34	S			S	S	S	S	S
	2-23	S			S	S	S	S	S
	2-10	S			S	S	S	S	S
	2-0	S							S
	1-TOP	S			S				S
	1-58	S			S	S	S	S	S
	1-46	S			S	S	S	S	S
	1-34	S			S	S	S	S	S
	1-23	S,W	W	S,W	S,W	S,W	S,W	S,W	S,W
	1-10	S,W	W	S,W	S,W	S,W	S,W	S,W	S,W
	1-0	S,W	W	W	W	W	W	W	S,W

S – soil sampled

W – water sampled

Airflow rates are for bioventing and biosparging columns. The flow rate in natural attenuation column was always 0 scm.

A sample from the barrel of contaminated water used in the study was substituted for water samples shown on 8/29/97. This sample represents the initial water concentration for each treatment period.

The 9/1/97 samples represent the end of the equilibration period.

approximately 30 g. Soil samples taken at all other sample intervals were between 1 to 3 g to minimize the effect of sampling on the behavior of soil columns.

Soil was collected from each port by removing the Teflon plug and collecting the soil sample with a spatula. The soil samples were taken from a location approximately 2.5 cm (1 in.) behind the surface of the soil in each port and placed in sampling jars. After all soil samples were taken, they were placed in a freezer until extractions for TPH and fatty acids could be performed.

Analytical Methods. Water samples were analyzed by EPA Method SW846-8260A for VOCs and by EPA Method SW846-8270B for PAHs.¹

The same analytical methods for rTPH and biomass described in Chapter 2, Phase I, "Microcosm Scale Evaluation," were used in the column evaluations.

¹ USEPA. (1992). op cit.

Results and Discussion

Heterogeneity between the different soil cores

Vertical profiles of rTPH concentrations in the three soil columns (bioparging, bioventing, and natural attenuation columns) are presented in Figure 15. These contamination profiles are qualitatively similar to each other and to the profile observed in the core collected from Area 1795 in March 1997 (Figure 7). However, each of these cores is quantitatively very different from the others, reflecting the heterogeneous nature of hydrocarbon contamination at this location. In each case, rTPH contamination is confined to a narrow region of approximately 0.6 m (2 ft). The contamination profiles seen in these columns fits the description of the "smear zone" described in the contamination assessment report by EA Engineering.¹ Contamination levels were highest in the bioventing column with a maximum rTPH concentration of approximately 8,000 ppm detected at port 1-23 which corresponds to approximately 4 m (12 ft) below

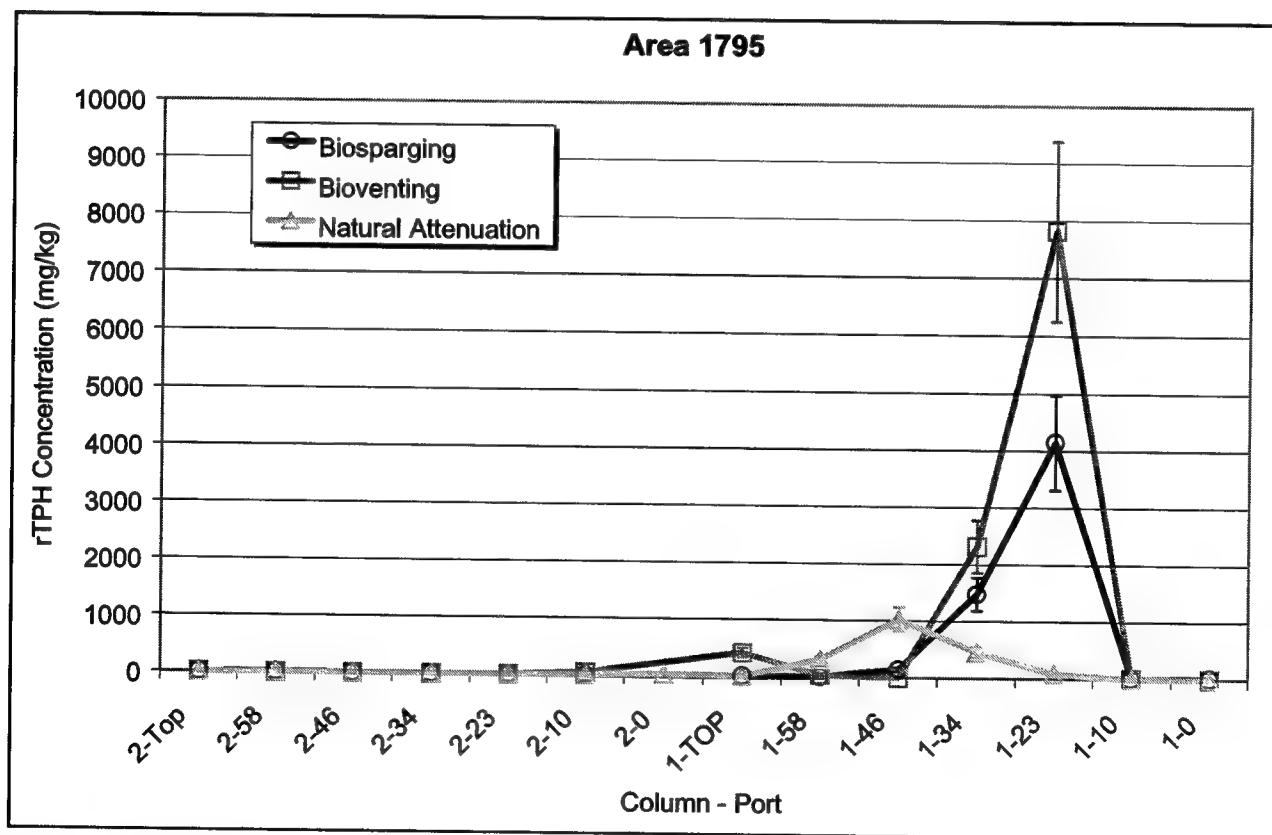


Figure 15. Initial soil rTPH concentrations in cores

¹ EA Engineering, Science and Technology. (1997). "Comprehensive contaminant assessment report—Volume III, Area 1595, Gasoline Alley, Fort Drum, New York.

ground surface (Table 5). rTPH contamination levels were much lower in the natural attenuation column with a maximum of 1,000 ppm occurring approximately 0.6 m (2 ft) higher in the column than that seen in the bioventing and the biosparging column.

The quantitative heterogeneity of the cores was evident in terms of microbial analysis also. The estimates of viable biomass (PLFA) from each of the three cores are shown in Figure 16 as a function of depth. Again, as in the rTPH contamination profiles, the vertical profile of biomass in the soil columns was qualitatively very similar but different quantitatively. There is an increase in biomass in the subsurface in the region of the rTPH contamination that suggests a contaminant influence on biological activity.

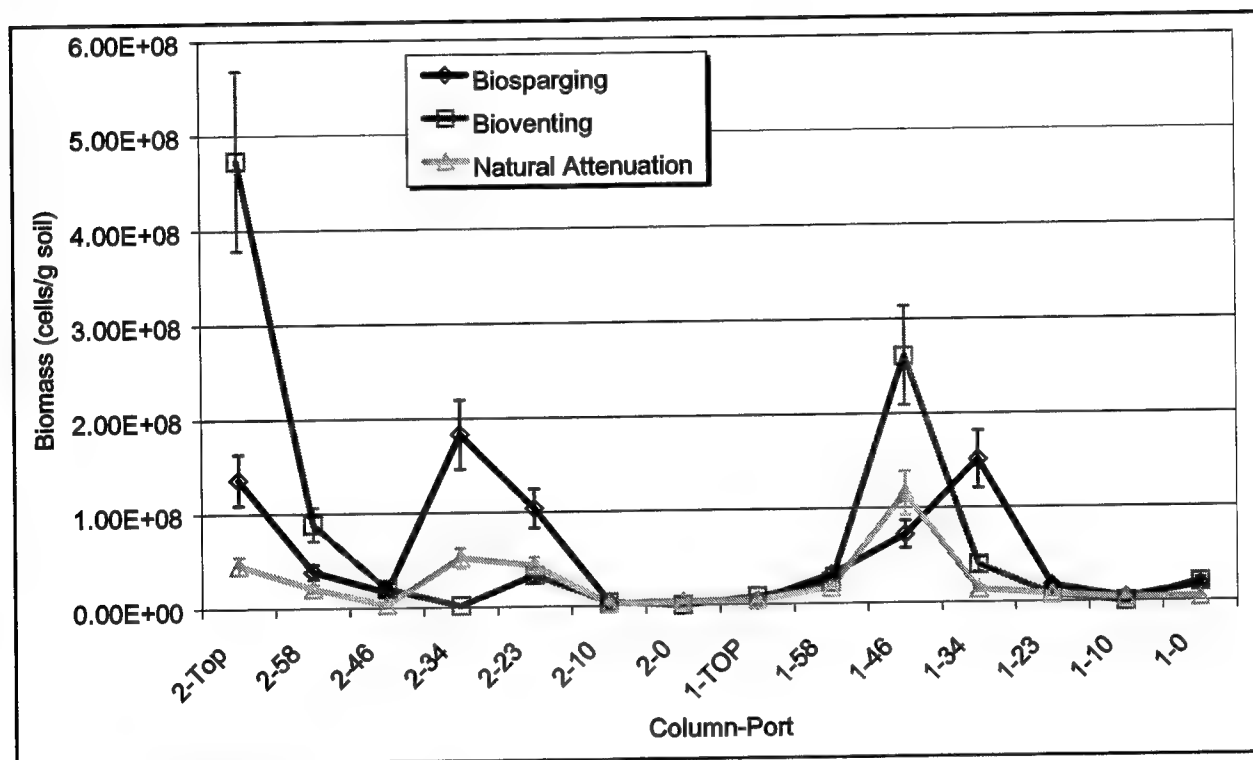


Figure 16. Initial biomass in cores

Microbial responses to engineered bioremediation strategies

Total viable microbial biomass remained fairly constant over the time course under all three remediation regimes; air-sparging, bioventing, and natural attenuation (Table 7). Slight increases in total biomass were observed under the bioventing and natural attenuation regimes at specific locations throughout the test columns. A simple breakdown of lipid biomarkers revealed that the two aggressive treatments did have different effects on microbial abundance (Table 7).

The total microbial biomass, for the lower halves of the soil columns, were summed and divided into five descriptive classes. Assuming that the natural attenuation column most closely approximates insitu conditions, the unamended

Table 7
Total Bacterial Biomass (pmol PLFA g⁻¹ soil) of Five Bacterial Classifications in Soil Columns Representing Three Bioremediation Treatments

Bacterial Classification	Natural attenuation		Biosparging		Bioventing	
	Initial	Final	Initial	Final	Initial	Final
Gram-positive	213	493	401	1,078	1,410	448
Gram-negative	3,251	5,228	4,797	4,694	4,122	4,924
Actinomycete	2	15	29	2	108	33
SRB/IRB	0	700	46	4	805	82
Fungi	0	153	27	21	260	259

microbiota exhibited the following pattern: Gram-positive bacteria increased two-fold, Gram-negative bacteria increased by one and a half, both fungal and actinomycete biomarkers became apparent, and an increase of sulfate reducing/iron reducing bacteria biomarkers was measured. In short, total unamended microbial populations increased in biomass over the incubation period. In contrast, the air-sparging treatment showed a substantial increase only in the Gram-positive bacterial populations (~2-fold), while the bioventing treatment appears to have induced an increase only in the Gram-negative bacterial biomass (~1-fold). The influence of O₂ on the extant microbiota was quite apparent. Biomass of the reducing bacterial populations (SRB/IRB) decreased under the two aeration regimes and increased slightly with the natural attenuation treatment. The different effects the two remediation treatments have on the extant biota can certainly be related to differences in the modes of oxygen delivery and resulting oxygen bioavailability.

These results are consistent with the community relationships identified for the Area 1595 microbiota with respect to rTPH concentration. A community containing substantial biomass of both aerobic Gram-positive and Gram-negative bacterial populations was identified as being correlated to TPH loss.

Natural attenuation

All data developed from the natural attenuation column are provided in Appendix B.

Soil phase rTPH and biomass concentrations. The rTPH concentration profiles in the natural attenuation column at the beginning and at the end of the experiment (9 weeks) are shown in Figure 17. On the whole, the rTPH profile in the column remained unchanged over this time period. The same was observed in the soil samples collected at intermediate time points (not shown). The differences between the rTPH concentrations at the area of highest contamination can be attributed to analytical uncertainty. In only one location was there a significant reduction of rTPH concentration in the soil. This reduction occurred

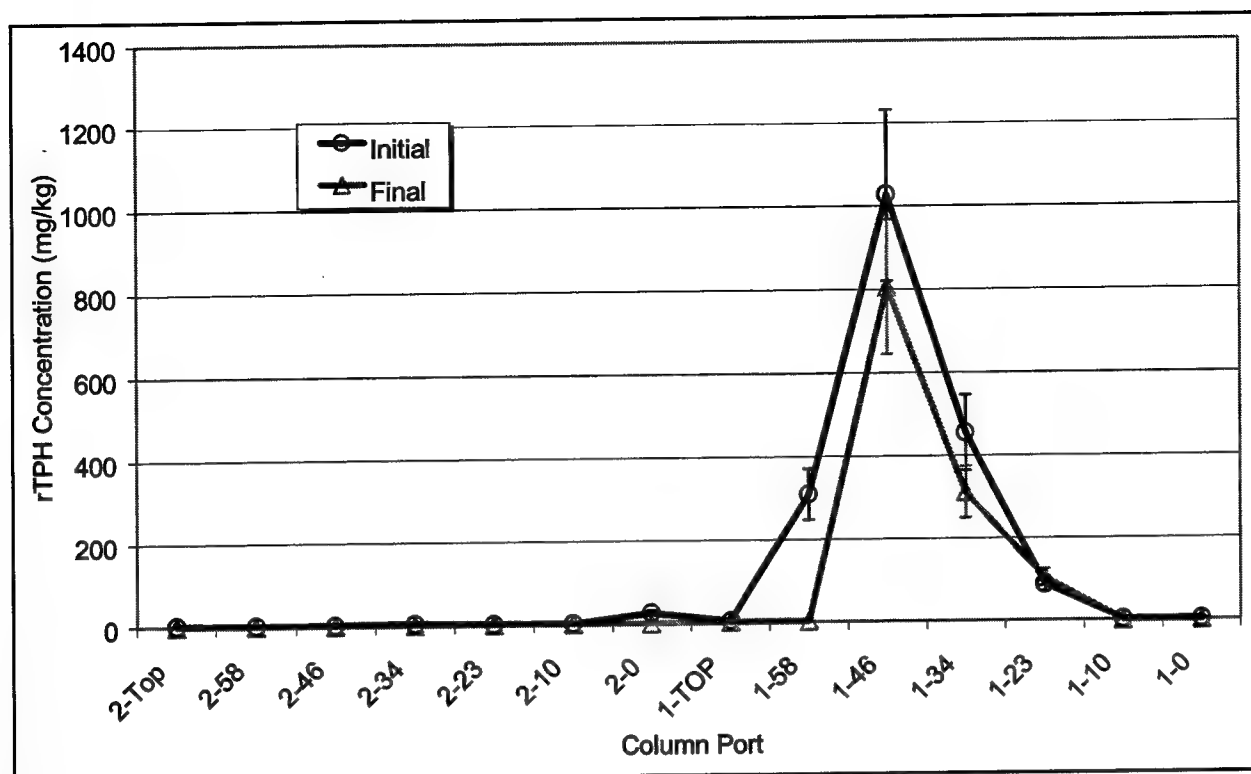


Figure 17. Initial and final soil rTPH concentrations – natural attenuation

at port 1-58, which appeared to be the top of the contamination “smear zone” in the soil column.

The total rTPH present in the column at the beginning of the experiment was 4.8 g ($\sigma = 1.0$). rTPH in the column at the end of the 9-week treatment period was measured to be 3.2 g ($\sigma = 0.6$). These data were based on analysis of 30-g samples of soil collected from each port (Table 6) at the beginning and end of the experiment. It can only be said with 92 percent confidence that there was a change in the total rTPH in the column over the duration of the evaluation. Analyses of 1-g intermediate point samples resulted in significantly larger variations in total rTPH in the column and no trend was discernible.

Although a confidence level of 95 percent is normally preferred, a total removal rate of TPH from the column was calculated using the initial and final rTPH in the columns for the sake of comparison to the other treatments evaluated. The zero-order (concentration independent) rate was calculated to be 2.5-mg rTPH/kg contaminated soil/day. This removal rate is based on the estimated mass of contaminated soil in the column. A gross estimate of the time required for removal of the contamination can be achieved by dividing the highest concentration of rTPH on the soil by this rate.

The biomass concentration profiles at the initial and end points of the natural attenuation evaluation are shown in Figure 18. Biomass appeared to increase significantly in and just above the saturated zone of the column. This increase in biomass corresponds to the area of high TPH concentration and may be due to

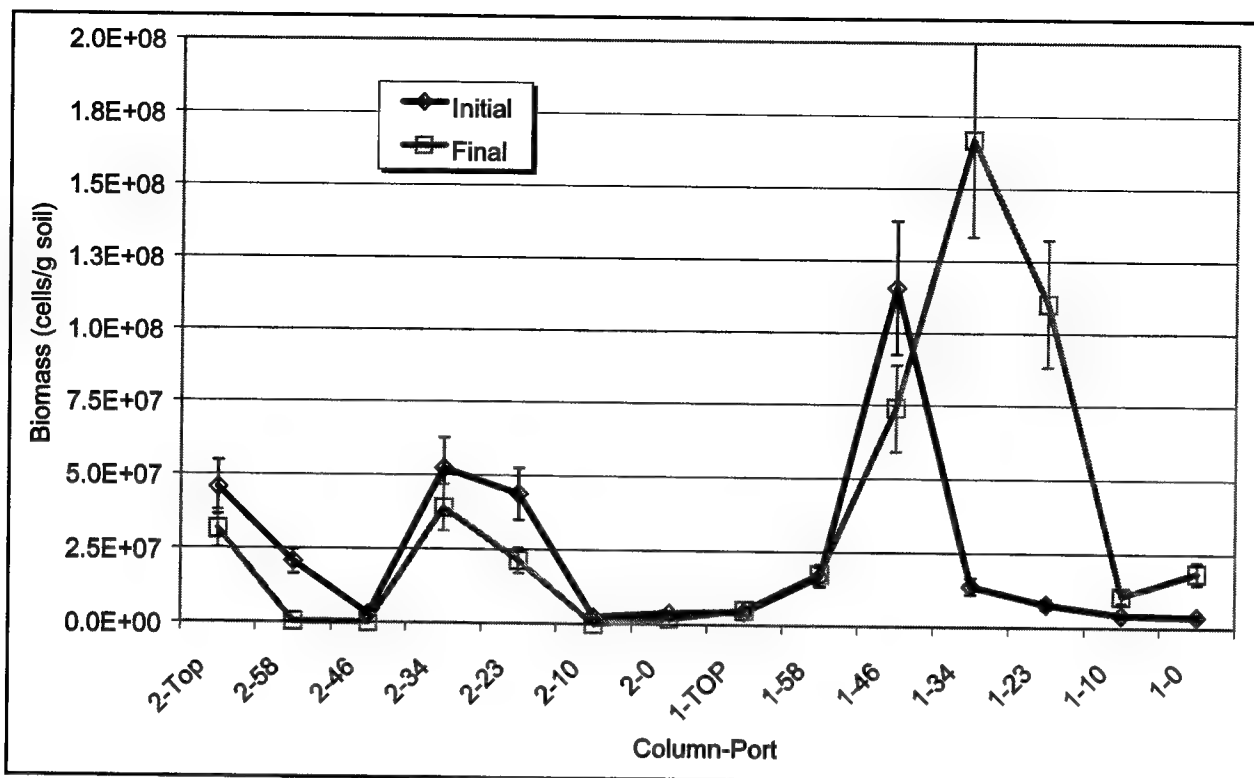


Figure 18. Initial and final biomass in soil – natural attenuation

the addition of a small amount of oxygen during the exchanges of water during sampling periods.

Aqueous phase rTPH concentrations. Total petroleum hydrocarbon concentration in water samples from the bottom, middle, and top of the saturated zone for each treatment period are illustrated in Figure 19 and listed in Table 8. As described in Chapter 3, paragraph “Water sampling method,” the saturated zone was drained at the end of each sampling period. Contaminated groundwater from the site was then added to the column. This water sampling method simulated the movement of groundwater through a specific aquifer zone and avoided cross contamination between the saturated zone levels during water sampling. Any change in the aqueous contaminant concentration during a treatment period is the cumulative result of interactions between groundwater and contaminated soil, and of any biotic and abiotic processes taking place over the treatment period.

The results from the equilibration period, ending September 1, suggest a redistribution of hydrocarbons between the soil and aqueous phases. Any redistribution however, did not change the concentration of rTPH in the soil substantially, as there was approximately two orders of magnitude greater mass of rTPH in the soil as there was in the aqueous phase.

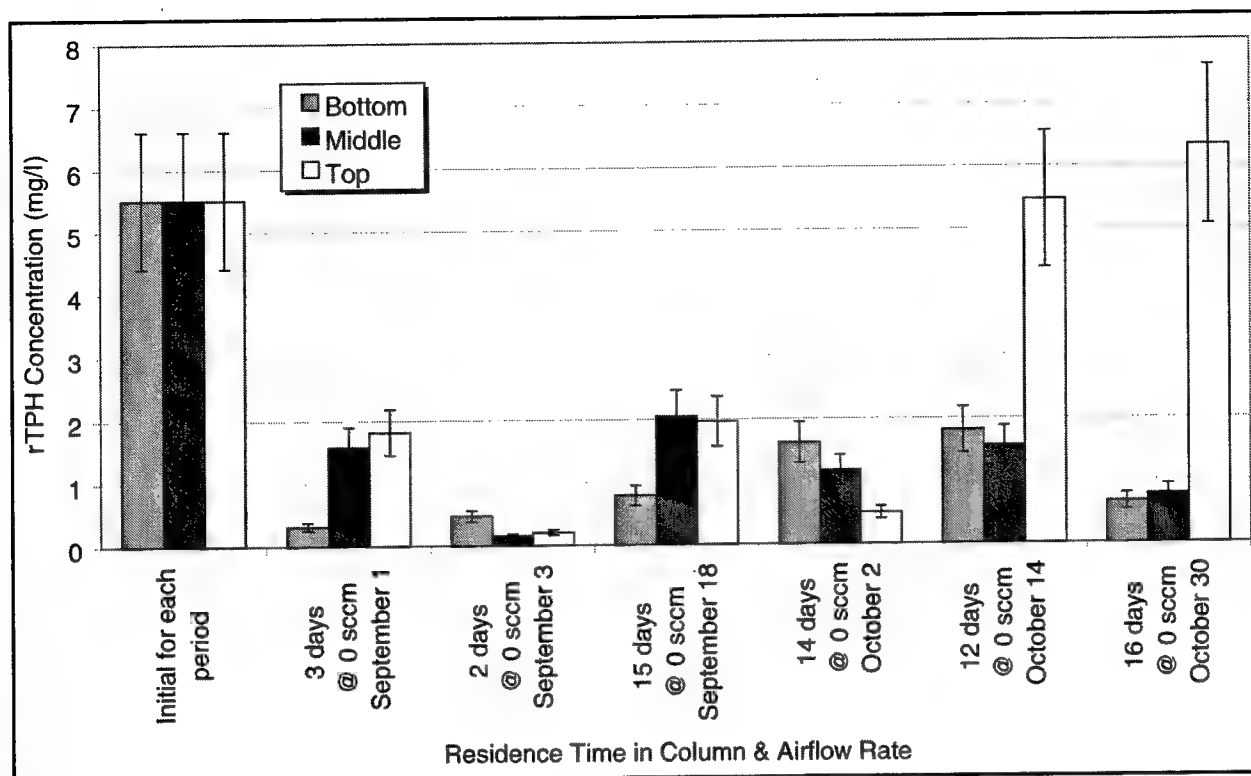


Figure 19. rTPH concentration in water – natural attenuation

Table 8
rTPH Concentration In Water – Natural Attenuation

Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration \pm 20% (mg/l)			
			Initial	Final Bottom	Final Middle	Final Top
Sep 1	3	0	5.51	0.317	1.58	1.81
Sep 3	2	0	5.51	0.472	0.158	0.208
Sep 18	15	0	5.51	0.793	2.04	1.96
Oct 2	14	0	5.51	1.62	1.18	0.500
Oct 14	12	0	5.51	1.80	1.56	5.47
Oct 30	16	0	5.51	0.661	0.777	6.33

A different sampling procedure was used on September 3. During this anomalous sampling event, the water samples were drawn from the ports at a higher flow rate. It is believed that this resulted in significant volatilization of the contaminant from the sample. During the last two treatment periods, more water was added to each column to increase the amount of water recovered for analysis from the top of the saturated zone. The raised water level caused water in the top of the saturated zone to come into contact with soil containing significantly greater rTPH contamination. Unfortunately, the decision to add more water during the last two treatment periods made significant comparison between aqueous rTPH concentrations in the top of the saturated zone between these and earlier treatment periods impossible. For these reasons, the samples

from September 3 and October 14 and 30 were not considered in the analysis of aqueous TPH removal.

Analysis of the removal rate of rTPH from the aqueous phase requires that the continuous exchange of the contaminant between the sorbed and aqueous phase be taken into account. Because no sorption studies were conducted for the contaminant and soil matrix in this study, the rate of rTPH desorption from the soil was estimated from changes in the aqueous rTPH concentrations in the upper saturated zone during the initial 7-day equilibration period. The upper saturated zone was chosen because the soil in this area contained the highest level of rTPH contamination. The rate of rTPH desorption was estimated using Equation 1. Calculating the rate in this manner assumes that no loss of rTPH from the aqueous phase occurred during this time period. Undoubtedly there was some level of rTPH loss, either from volatilization or degradation, during this time period, therefore the rate of desorption calculated is conservative. The rate of desorption calculated in this manner is also specific to this location and should not be used at other locations in the contamination site. A partition coefficient and desorption-rate constant for the contaminant of concern and soil type at a site should be developed from desorption studies for modeling purposes. A desorption rate calculated in this manner, however, will allow an aqueous-rTPH removal-rate constant to be calculated which can be used to model contaminant transport at the site. Equation 1 is an example of a first-order desorption-rate constant and assuming that C_f at end of equilibration period is $0.90 \cdot C_e$:

$$\frac{dC}{dt} = -k_{dr}(C_e - C)$$

$$k_{dr} = -\frac{\ln \left| \frac{\frac{C_f}{0.90} - C_f}{\frac{C_f}{0.90} - C_i} \right|}{t_f - t_i} \quad (1)$$

where

k_{dr} = 1st order desorption-rate constant

C = TPH concentration in water

C_e = equilibrium TPH concentration in water

The desorption rate could not be calculated for the natural attenuation column because the concentration in the column decreased during the equilibration period. These data suggest that the concentration of rTPH in the soil was very low in the saturated zone, which is confirmed by rTPH analysis of the soil (Figure 17). Unfortunately, because a desorption-rate constant for aqueous rTPH could not be calculated in the natural attenuation column, a removal-rate constant for aqueous rTPH could not be calculated either. However, cursory observations from the data suggest that removal of rTPH from

the aqueous phase was due primarily to adsorption to soil with little or no rTPH contamination. The fact that there was no change in the extent of aqueous rTPH reduction between the short 3-day equilibration period and the longer (approximately 2-week) treatment periods that followed suggests that biological activity in the saturated zone was low.

Exit gas analysis. No gas was introduced into this column. Therefore, off-gases could not be collected for analysis. The analysis of the traps at the exit of the column did not give any information concerning the volatilization losses, nor of any mineralization losses evidenced from exit gas analysis.

Bioventing

All data developed from the bioventing column are provided in Appendix C.

Soil phase, rTPH and biomass concentrations. The bioventing evaluation was conducted by introducing air into the column above the saturated zone through sampling port 1-34. Air was introduced to the column on day 3, after sampling the equilibration period. The results of the initial and final soil-rTPH and biomass measurements from this column are shown in Figure 20 and 21, respectively. These results are from analyses conducted with large, 30-g, soil

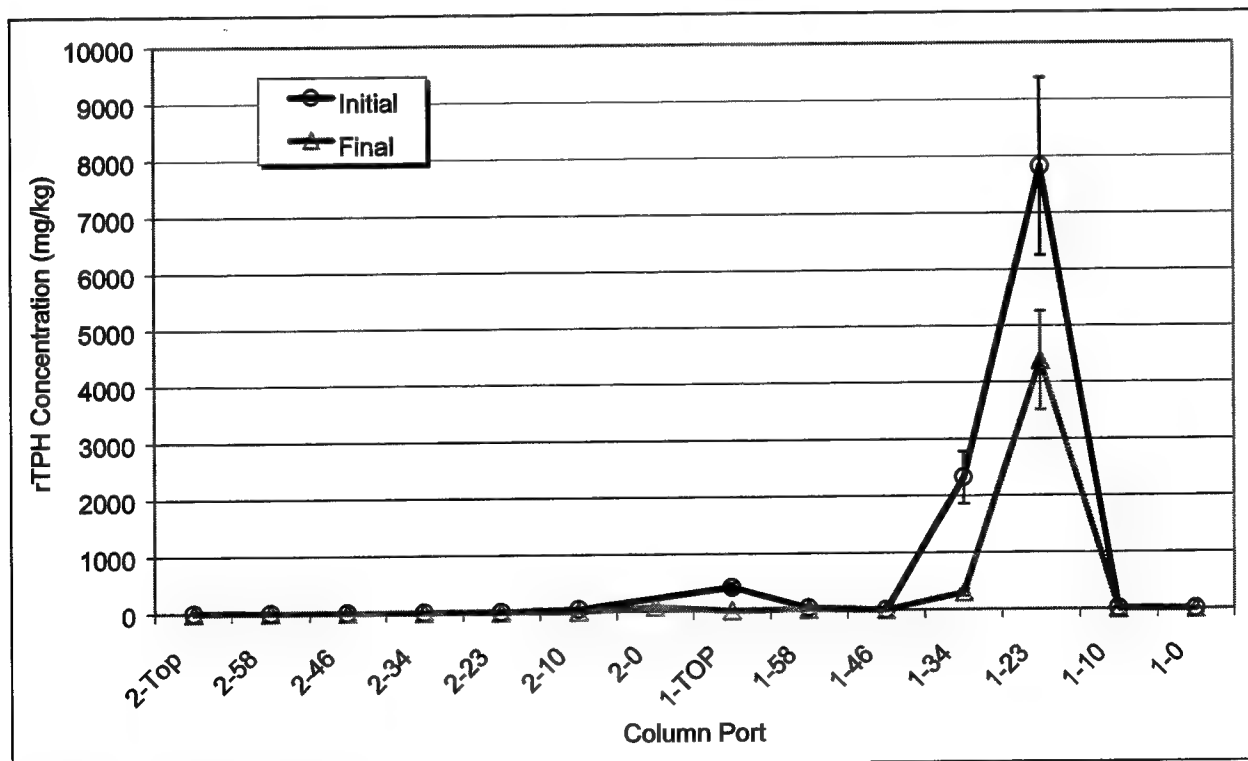


Figure 20. Initial and final soil rTPH concentrations – bioventing

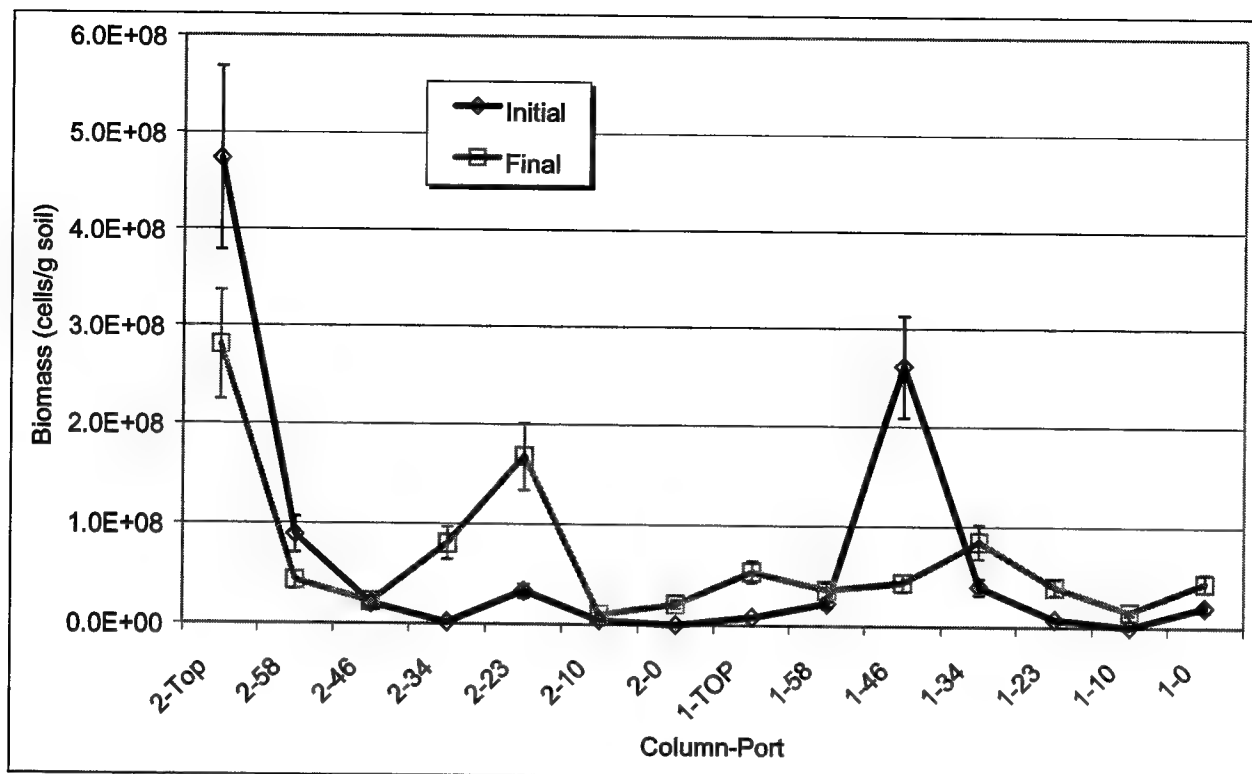


Figure 21. Initial and final biomass in soil - bioventing

samples collected from each port at the beginning of the experiment and at the completion of 8-½ weeks of bioventing, 9 weeks after the beginning of the experiment.

A mass balance of rTPH in the column showed the presence of 27.1 g ($\sigma = 5.4$) at the start of the experiment and 12.3 g ($\sigma = 2.5$) at the end. It can be said with 99 percent confidence that there was a decrease of total rTPH in the column during the duration of the evaluation. Bioventing of the soil column appears to have resulted in a reduction of rTPH in the column of 14.8 g with a 95 percent confidence interval from 5.0 to 24.6. Analysis of 1-g soil samples from intermediate time points shows a large deviation in rTPH in the column and no trend was discernible.

For the sake of comparison to the other treatments evaluated, a total removal rate of TPH from the column was calculated using the initial and final rTPH in the columns. The zero-order (concentration independent) rate was calculated to be 17.5-mg rTPH/kg contaminated soil/day. This removal rate is based on the estimated mass of contaminated soil in the column. A gross estimate of the time required for removal of the contamination can be achieved by dividing the highest concentration of rTPH on the soil by this rate.

The biomass data presented in Figure 21 shows a significant increase in the biomass in most areas of the column. These increases occurred in many areas where TPH contamination was not detected. This microbial growth may have been supported by volatilized petroleum hydrocarbons from lower in the column.

Some form of growth substrate other than petroleum hydrocarbons may also have supported microbial growth which was stimulated by the addition of air to the column.

Aqueous phase rTPH concentrations. Total petroleum hydrocarbon concentration in water samples from the bottom, middle, and top of the saturated zone for each treatment period are illustrated in Figure 22 and listed in Table 9. As described in this chapter, paragraph "Water sampling method," the saturated zone was drained at the end of each sampling period. Contaminated groundwater from the site was then added to the column. This water sampling method simulated the movement of groundwater through a specific aquifer zone and avoided cross contamination between the saturated zone levels during water sampling. Any change in the aqueous contaminant concentration during a treatment period is the cumulative result of interactions between groundwater and contaminated soil and of any other biotic and abiotic processes taking place over the treatment period.

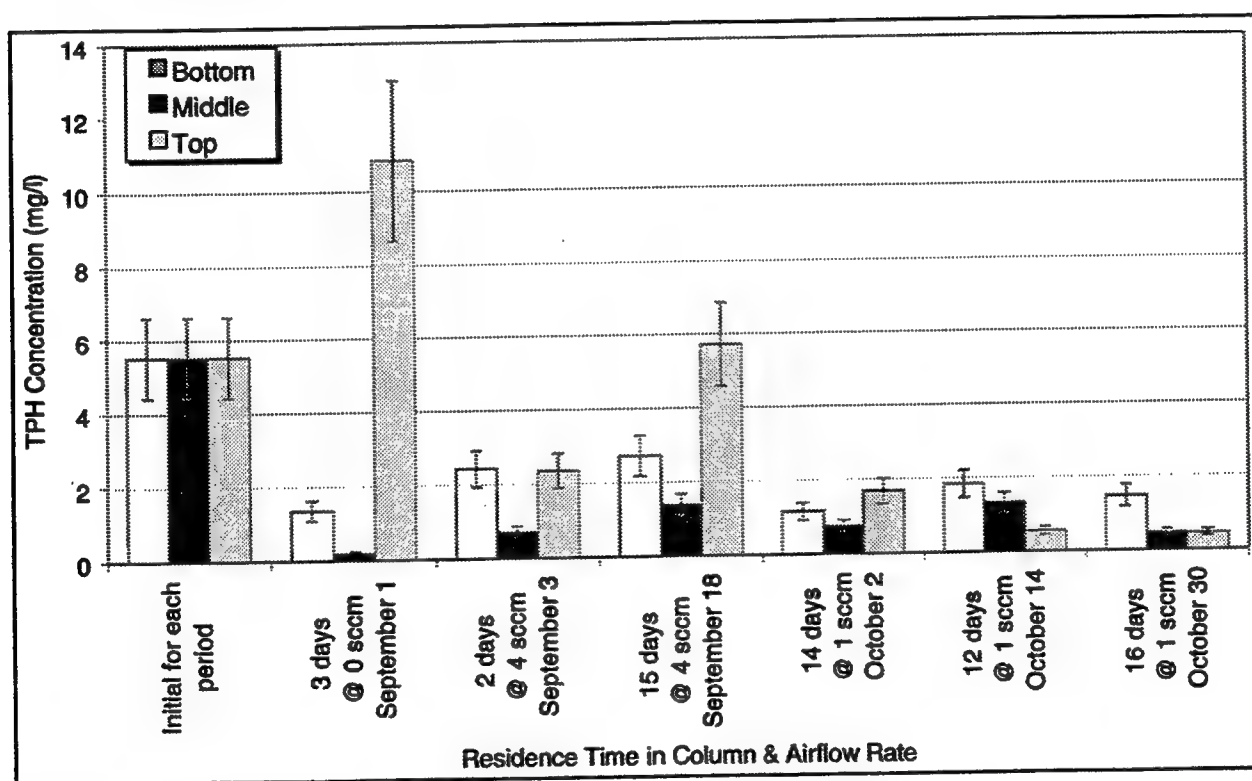


Figure 22. rTPH concentration in water – bioventing

The results from the equilibration period ending September 1 suggest a redistribution of hydrocarbons between the soil and aqueous phases. Any redistribution, however, did not change the concentration of rTPH in the soil significantly, since there was approximately two orders of magnitude greater mass of rTPH in the soil than in the aqueous phase. During the initial 3-day equilibration period, no air was forced into the soil column. The increase of aqueous-rTPH concentration in the top of the saturated zone was the result of

Table 9 rTPH Concentration in Water - Bioventing						
Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration \pm 20% (mg/l)			
			Initial	Final Bottom	Final Middle	Final Top
Sep 1	3	0	5.51	1.35	0.207	10.8
Sep 3	2	4	5.51	2.42	0.725	2.34
Sep 18	15	4	5.51	2.71	1.39	5.71
Oct 2	14	1	5.51	1.16	0.762	1.68
Oct 14	12	1	5.51	1.84	1.34	0.555
Oct 30	16	1	5.51	1.47	0.477	0.463

equilibration with soil containing a high-contaminant concentration. The decrease of aqueous-rTPH concentrations in the middle and bottom of the saturated zone was evidence of adsorption of aqueous rTPH to soil with little or no rTPH contamination as shown in Figure 20, port 1-10 and 1-0.

A different sampling procedure was used on September 3. During this anomalous sampling event, the water samples were drawn from the ports at a higher flow rate. It is believed that this resulted in significant volatilization of the contaminant from the sample. For this reason, the samples from September 3 were not considered in the analysis of aqueous rTPH removal.

Analysis of the removal rate of rTPH from the aqueous phase requires that the continuous exchange of the contaminant between the sorbed and aqueous phase be taken into account. Because no sorption studies were conducted for the contaminant and soil matrix in this study, the rate of rTPH desorption from the soil was estimated from changes in the aqueous-rTPH concentrations in the upper saturated zone during the initial 3-day equilibration period. The upper saturated zone was chosen because the soil in this area contained the highest level of rTPH contamination and was therefore the area of highest significance to the study. The rate of rTPH desorption was estimated using Equation 1. The first-order desorption rate constant calculated for the bioventing column was 0.563 day^{-1} . Calculating the rate in this manner assumes that no loss of TPH from the aqueous phase occurred during this time period. Undoubtedly there was some level of rTPH loss, from volatilization or degradation, during this time period, therefore the rate of desorption calculated is conservative. The rate of desorption calculated in this manner is also specific to this location and should not be used at other locations in the contamination site. A partition coefficient and desorption-rate constant for the contaminant of concern and soil type at the site should be developed from desorption studies for modeling purposes. The desorption rate calculated here, however, allows an aqueous-rTPH removal-rate constant to be calculated, which can be used to model contaminant transport at the site.

Utilizing the desorption-rate constant calculated from the equilibrium period and the average change between the initial and final aqueous-rTPH concentrations in the upper saturated zone, a first-order removal-rate constant was calculated for the treatment periods following the equilibration period

utilizing Equation 2. This calculation assumes that a steady aqueous-rTPH concentration was reached by the end of each treatment period (i.e., the rate of desorption is equal to the rate of removal). The average removal-rate constant calculated, excluding the anomalous data point on September 3, was 2.65 day⁻¹ (Equation 2).

$$\frac{dC}{dt} = k_{dr} (C_e - C) - k_r C \quad (2)$$

where

k_r = 1st order rTPH removal-rate coefficient

$$\text{Assuming } \frac{dC}{dt} = 0 \rightarrow k_r = \frac{k_{dr}(C_e - C)}{C}$$

Exit gas analysis. Air was initially introduced to the column at a flow rate of 4 sccm. After 2-½ weeks, the flow rate of air into the column was reduced to 1 sccm. An airflow rate of 1 sccm corresponds to an estimated specific flow rate of 49-scc air/kg soil/day, an average linear velocity of approximately 5.6 cm/hr, and an estimated 60-hr residence time in the soil.

The analysis of oxygen and carbon dioxide in the exit gas showed signs of significant biological activity in the column. As air was passed through the column, the volume fraction of oxygen decreased while the volume fraction of carbon dioxide increased. The measured volume fractions of oxygen and carbon dioxide in the inlet and exit gases passing through the bioventing column are presented in Figure 23. These respiration data are clearly indicative of biological activity in the column.

The cumulative consumption of oxygen and production of carbon dioxide were calculated from airflow rates and of compositions of inlet and exit gases. Calculations of oxygen consumption and carbon dioxide production were based on Equations 3 and 4, respectively. The cumulative oxygen consumption and carbon dioxide production data are shown in Figure 24. Since there is a well defined relationship between aerobic hydrocarbon metabolization and oxygen consumption of 3.2 g oxygen per gram hydrocarbon,¹ the data in Figure 24 can be converted into cumulative biodegradation of TPH. Over the 8-½ weeks of bioventing, the total mass of contaminant degraded, calculated from oxygen consumption data, is 1.68 g. Looking at Figure 24, a steady rate of oxygen consumption and carbon dioxide production was reached and can be seen from day 42 to 58. From these data, a steady oxygen consumption rate of 0.40 (σ = 0.002) mmole/day and a steady carbon dioxide production rate of 0.32 (σ = 0.004) mmole/day were calculated. The estimated mass of contaminated

¹ T. J. Cookson. (1995). *Bioremediation engineering—Design and application*. McGraw Hill, New York.

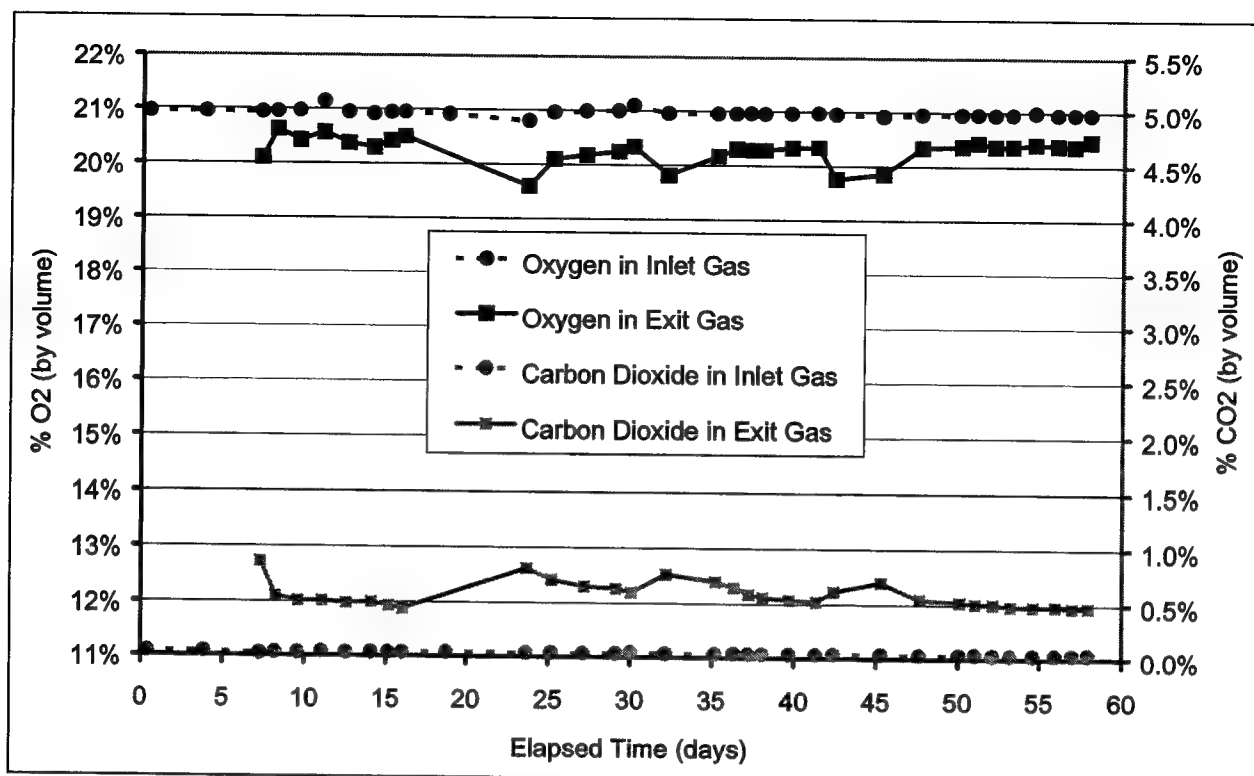


Figure 23. Inlet and outlet O₂ and CO₂ concentrations – bioventing

soil in the column was 14.6 kg. The corresponding zero-order rate of hydrocarbon

$$\Delta O_2 = \frac{Q}{22,400} \left[O_2^{in} - O_2^{out} \left(\frac{1 - O_2^{in} - CO_2^{in}}{1 - O_2^{out} - CO_2^{out}} \right) \right] \frac{\Delta t}{1,440} \quad (3)$$

where

Q = airflow rate in standard cubic centimeters per minute

Δt = elapsed time in days

O_2 = molar fraction of oxygen

CO_2 = molar fraction of carbon dioxide

$$22,400 = \frac{\text{standard cm}^3}{\text{mole}}$$

$$1,440 = \frac{\text{minutes}}{\text{day}}$$

$$\Delta O_2 = \frac{Q}{22,400} \left[CO_2^{out} - CO_2^{in} \left(\frac{1 - O_2^{in} - CO_2^{in}}{1 - O_2^{out} - CO_2^{out}} \right) \right] \frac{\Delta t}{1,440} \quad (4)$$

where

Q = airflow rate in standard cubic centimeters per minute

Δt = elapsed time in days

O_2 = molar fraction of oxygen

CO_2 = molar fraction of carbon dioxide

$$22,400 = \frac{\text{standard cm}^3}{\text{mole}}$$

$$1,440 = \frac{\text{minutes}}{\text{day}}$$

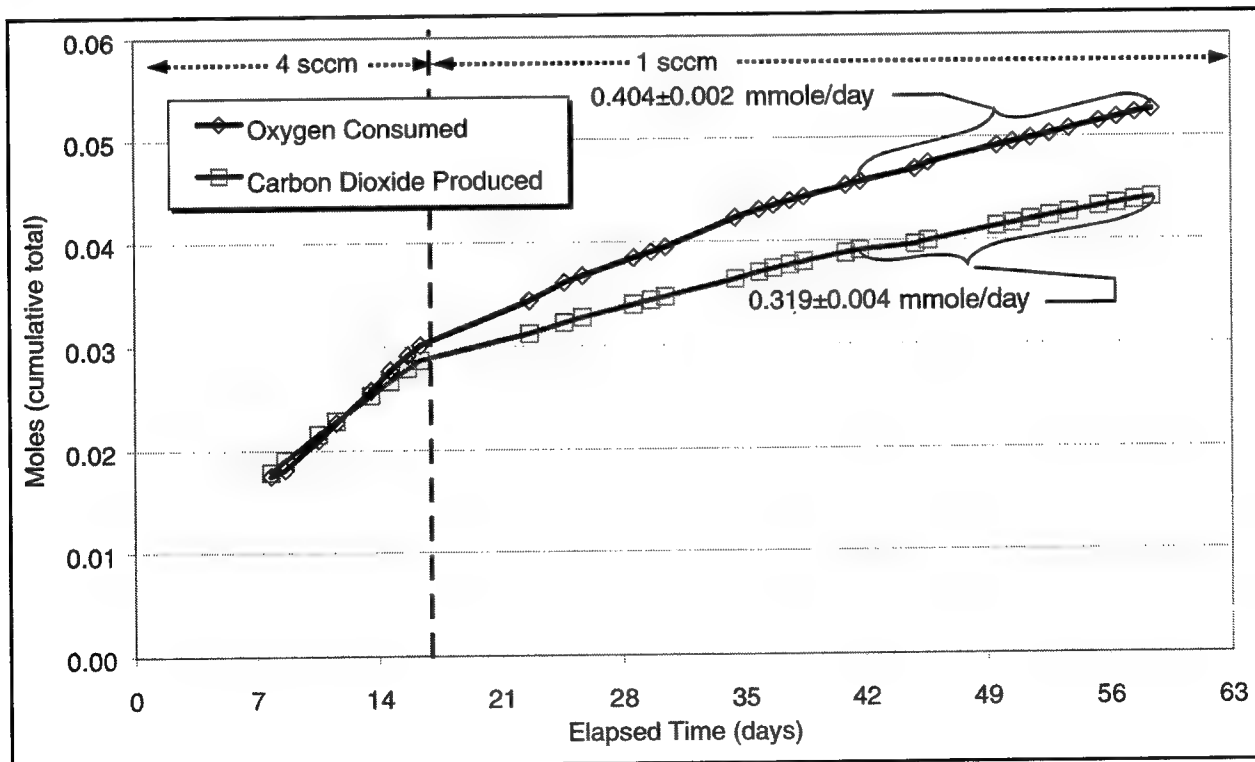


Figure 24. Cumulative O_2 consumption and CO_2 production vs time – bioventing

biological degradation from day 42 to 58 was 0.27 mg hydrocarbon kg contaminated soil⁻¹ day⁻¹.

A comparison of exit gas data (Figure 23) under the two different airflow rates appears to suggest a benefit from blowing air at a higher rate than the guidance given in the EPA Manual.¹ However, results from an identical evaluation of Area 1595 showed that the respiration rate decreased at approximately the same elapsed time in the evaluation. It is believed that the reduction of the respiration rate coinciding with the reduction of the airflow is a coincidence in this evaluation and that the respiration in the column would have settled at the same constant rate under both airflow rates. Evaluation of the oxygen content in the exit gas suggests that oxygen availability was never a limiting factor in the column for biological respiration. Therefore, we suggest that there is little benefit from blowing air at a higher rate than the EPA guidance.

The ratio of the carbon dioxide production rate and oxygen consumption rate is known as the respiration quotient (RQ). The characteristic value of RQ is dependent upon the nature of the substrate being metabolized by the cells. When carbohydrates are the substrate of interest, RQ values around 1.0 are generally observed under aerated conditions. Under the same conditions, metabolism of hydrocarbons yields RQ values around 0.67. For the bioventing column, an RQ value of 0.79 was observed suggesting hydrocarbon metabolism.

The calculated amount of TPH degraded based on respiration data (1.68 g) accounts for only a small fraction of the TPH removal measured in the soil column (14.8 ± 9.8 g). Based on these data and the lack of reliable analysis of VOCs in the exit gas, it is assumed that the remainder of the TPH removed from the column was lost through volatilization. This suggests that volatilization was the most significant pathway for rTPH removal in the column. This result is not surprising given the volatility of the major compounds comprising unleaded gasoline.

Biosparging

All data developed from the biosparging column are provided in Appendix D.

Soil phase rTPH and biomass concentrations. The biosparging evaluation was conducted by introducing air into the column in the saturated zone at the bottom of the column (port 1-0). Airflow was initiated beginning on day 3 after the equilibration period. The results of the initial and final soil-TPH and biomass measurements from this column are shown in Figures 25 and 26, respectively. These results are from analyses conducted with large, 30-g, soil samples collected from each port at the beginning of the experiment and at the completion of 8-½ weeks of biosparging, 9 weeks after the beginning of the experiment.

¹ USEPA. (1995). Op cit.

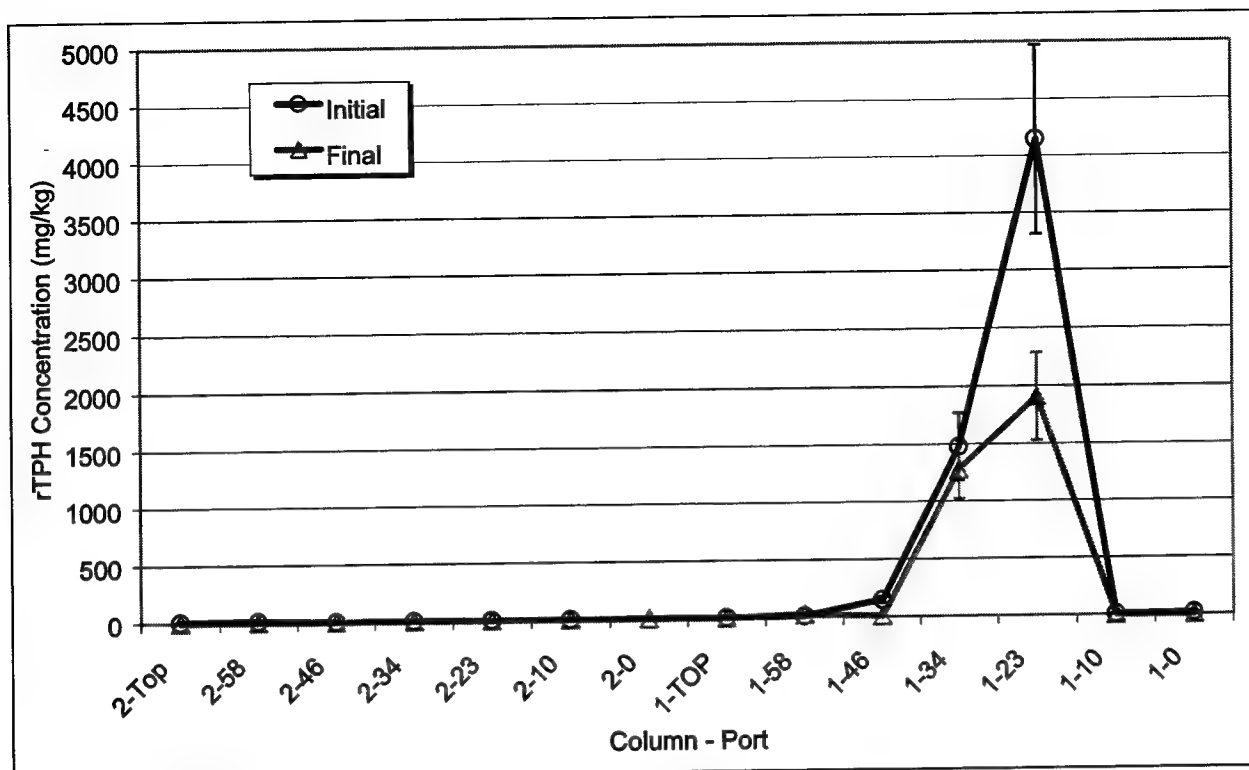


Figure 25. Initial and final soil rTPH concentrations – biosparging

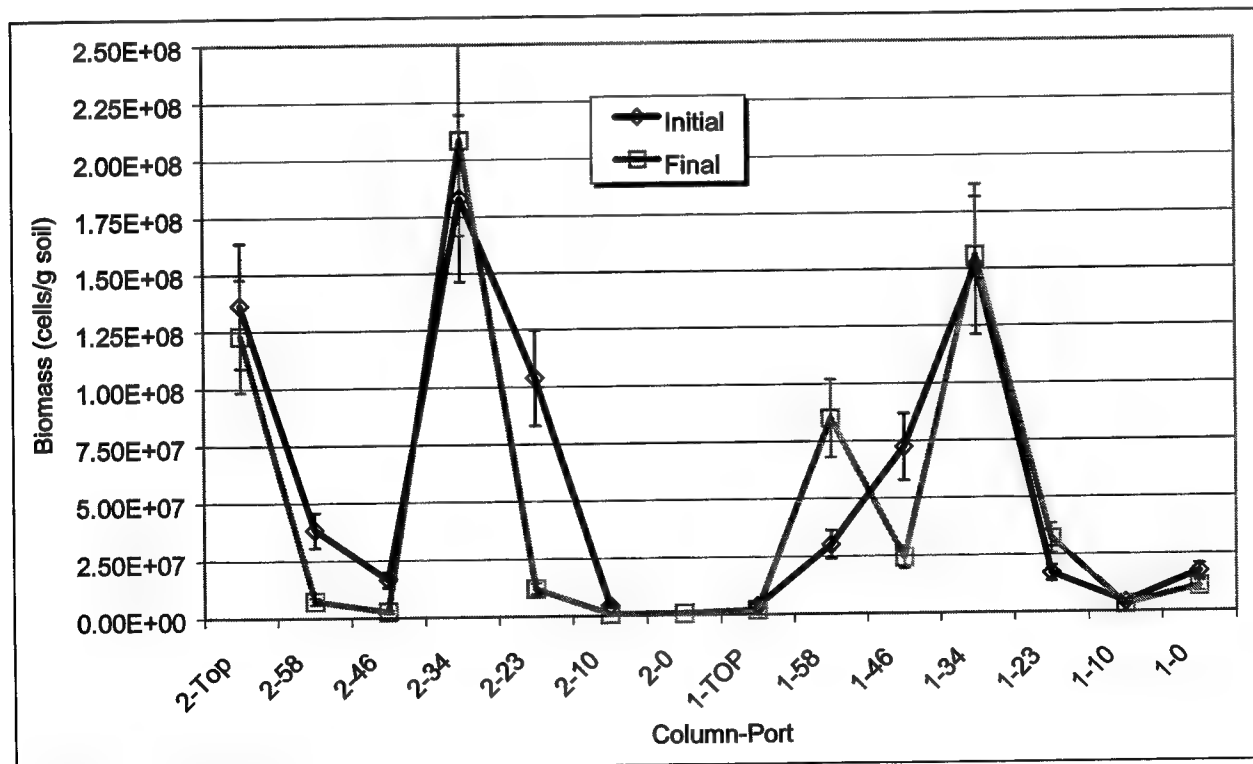


Figure 26. Initial and final biomass in soil – biosparging

A mass balance of rTPH in the column showed the presence of 15.0 g ($\sigma = 3.0$) at the start of the experiment and 8.4 g ($\sigma = 1.7$) at the end. It can be said with 97 percent confidence that there was a decrease of total rTPH in the column during the duration of the evaluation. Biosparging of the soil appears to have resulted in a reduction of rTPH in the column of 6.6 g with a 95 percent confidence interval from 0.9 to 12.3. Analysis of 1-g soil samples from intermediate time points shows a large deviation in rTPH in the column and no trend was discernible.

For the sake of comparison to the other treatments evaluated, a total removal rate of TPH from the column was calculated using the initial and final rTPH in the columns. The zero-order (concentration independent) rate was calculated to be 12.9-mg rTPH/kg contaminated soil/day. This removal rate is based on the estimated mass of contaminated soil in the column. A gross estimate of the time required for removal of the contamination can be achieved by dividing the highest concentration of rTPH on the soil by this rate.

Microbial biomass measurements (Figure 26) showed significant changes between the initial and final soil samples. However, no consistent relationship between changes in biomass and TPH could be seen in the column.

Aqueous phase rTPH concentrations. Total petroleum hydrocarbon concentration in water samples from the bottom, middle, and top of the saturated zone for each treatment period in 1997 are illustrated in Figure 27 and listed in

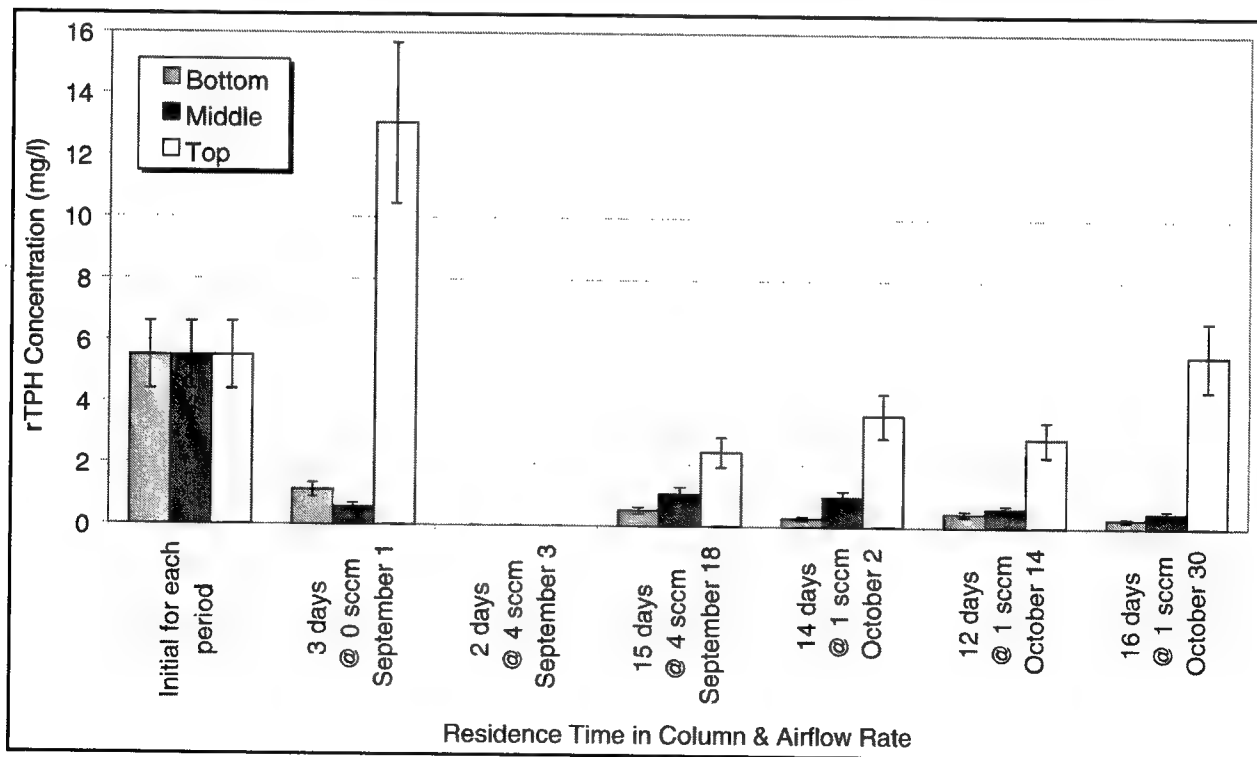


Figure 27. TPH concentration in water – biosparging

Table 10. As described in Chapter 3, paragraph "Water sampling method," the saturated zone was drained at the end of each sampling period. Contaminated groundwater from the site was then added to the column. This water sampling method simulated the movement of groundwater through a specific aquifer zone and avoided cross contamination between the saturated zone levels during water sampling. Any change in the aqueous contaminant concentration during the treatment period is the cumulative result of interactions between groundwater and contaminated soil and of any other biotic and abiotic processes taking place over the treatment period.

Table 10						
rTPH Concentration in Water – Biosparging						
Date, 1997	Residence Time, days	Aeration Rate, sccm	rTPH Concentration \pm 20% (mg/l)			
			Initial	Final Bottom	Final Middle	Final Top
Sep 1	3	0	5.51	1.14	0.589	13.1
Sep 3	2	4	5.51	0.000	0.000	0.000
Sep 18	15	4	5.51	0.506	1.06	2.41
Oct 2	14	1	5.51	0.285	0.972	3.63
Oct 14	12	1	5.51	0.452	0.605	2.87
Oct 30	16	1	5.51	0.280	0.486	5.59

The results from the equilibration period, ending September 1, suggest a redistribution of hydrocarbons between the soil and aqueous phases. Any redistribution, however, did not change the concentration of TPH in the soil significantly, as there was approximately two orders of magnitude greater mass of TPH in the soil as there was in the aqueous phase. During the initial 3-day equilibrium period, no air was forced into the soil column. The increase of aqueous-TPH concentration in the top of the saturated zone was the result of equilibration with soil containing a high-contaminant concentration. The decrease of aqueous-TPH concentrations in the middle and bottom of the saturated zone was evidence of adsorption of aqueous TPH to soil with little or no TPH contamination as shown in Figure 25 port 1-10 and 1-0.

A different sampling procedure was used on September 3. During this anomalous sampling event, the water samples were drawn from the ports at a higher flow rate. It is believed that this resulted in significant volatilization of the contaminant from the sample. For this reason, the samples from September 3 were not considered in the analysis of aqueous TPH removal.

Analysis of the removal rate of TPH from the aqueous phase requires that the continuous exchange of the contaminant between the sorbed and aqueous phase be taken into account. Because no sorption studies were conducted for the contaminant and soil matrix in this study, the rate of TPH desorption from the soil was estimated from changes in the aqueous TPH concentrations in the upper saturated zone during the initial 3-day equilibration period. The upper saturated zone was chosen because the soil in this area contained the highest level of TPH contamination and was therefore the area of highest significance to the study.

The rate of TPH desorption was estimated using Equation 1. The first-order desorption-rate constant calculated for the biosparging column was 0.608 day^{-1} . Calculating the rate in this manner assumes that no loss of TPH from the aqueous phase occurred during this time period. Undoubtedly there was some level of TPH loss, either from volatilization or degradation, during this time period, therefore the rate of desorption calculated is conservative. The rate of desorption calculated in this manner is also specific to this location and should not be used at other locations in the contamination site. A partition coefficient and desorption rate constants for the contaminant of concern and soil type at the site should be developed from desorption studies for modeling purposes. The desorption rate calculated here, however, allows an aqueous-TPH removal-rate constant to be calculated which can be used to model contaminant transport at the site.

Utilizing the desorption-rate constant calculated from the equilibrium period and the average change between the initial and final aqueous TPH concentrations in the upper saturated zone, a first-order removal-rate constant was calculated for the treatment periods following the equilibration period utilizing Equation 2. This calculation assumes that a steady aqueous-TPH concentration was reached by the end of each treatment period (i.e. the rate of desorption is equal to the rate of removal). The average removal-rate constant calculated, excluding the anomalous data point on September 3, was 1.82 day^{-1} .

Exit gas analysis. Air was initially introduced to the column at a flow rate of 4 sccm. After 2-½ weeks the flow rate of air into the column was reduced to 1 sccm. An air flow rate of 1 sccm corresponds to an estimated specific flow rate of 51-scc air/kg soil/day, an average linear velocity of approximately 5.6 cm/hr, and an estimated 58-hr residence time in the soil.

The analysis of oxygen and carbon dioxide in the exit gas showed signs of significant biological activity in the column. As air was passed through the column, the volume fraction of oxygen decreased while the volume fraction of carbon dioxide increased. The measured volume fractions of oxygen and carbon dioxide in the inlet and exit gases passing through the bioventing column are presented in Figure 28. These respiration data are clearly indicative of biological activity in the column.

The cumulative consumption of oxygen and production of carbon dioxide were calculated from airflow rates and of compositions of inlet and exit gases. Calculations of oxygen consumption and carbon dioxide production were based on Equations 3 and 4, respectively. The cumulative oxygen consumption and carbon dioxide production data are shown in Figure 29. Since there is a well defined relationship between aerobic hydrocarbon metabolization and oxygen consumption of 3.2 g oxygen per gram hydrocarbon,¹ the data in Figure 29 can be converted into cumulative biodegradation of rTPH. Over the 8-½ weeks of bioventing, the total mass of contaminant degraded, calculated from oxygen consumption data, is 2.46 g. Looking at Figure 29, a steady rate of oxygen consumption and carbon dioxide production was reached and can be seen from

¹ Cookson, . (1995). Op cit.

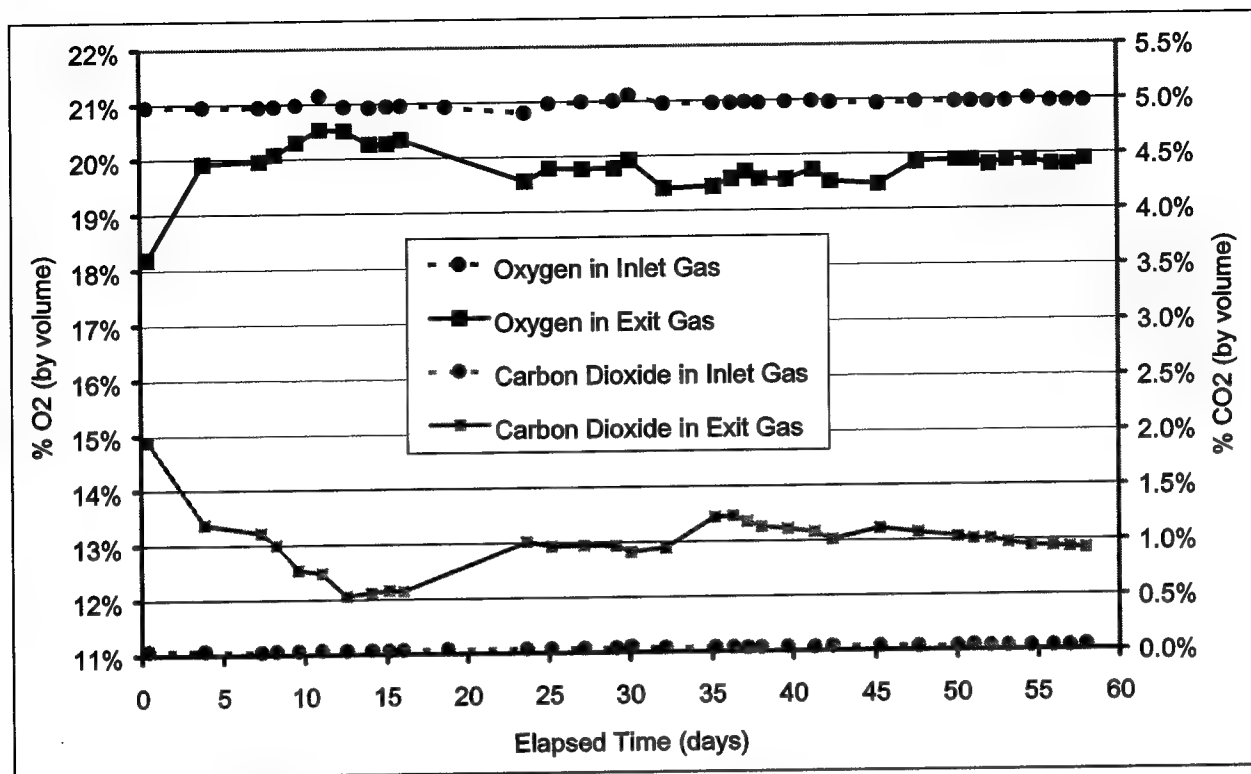


Figure 28. Inlet and outlet O₂ and CO₂ concentrations – biosparging

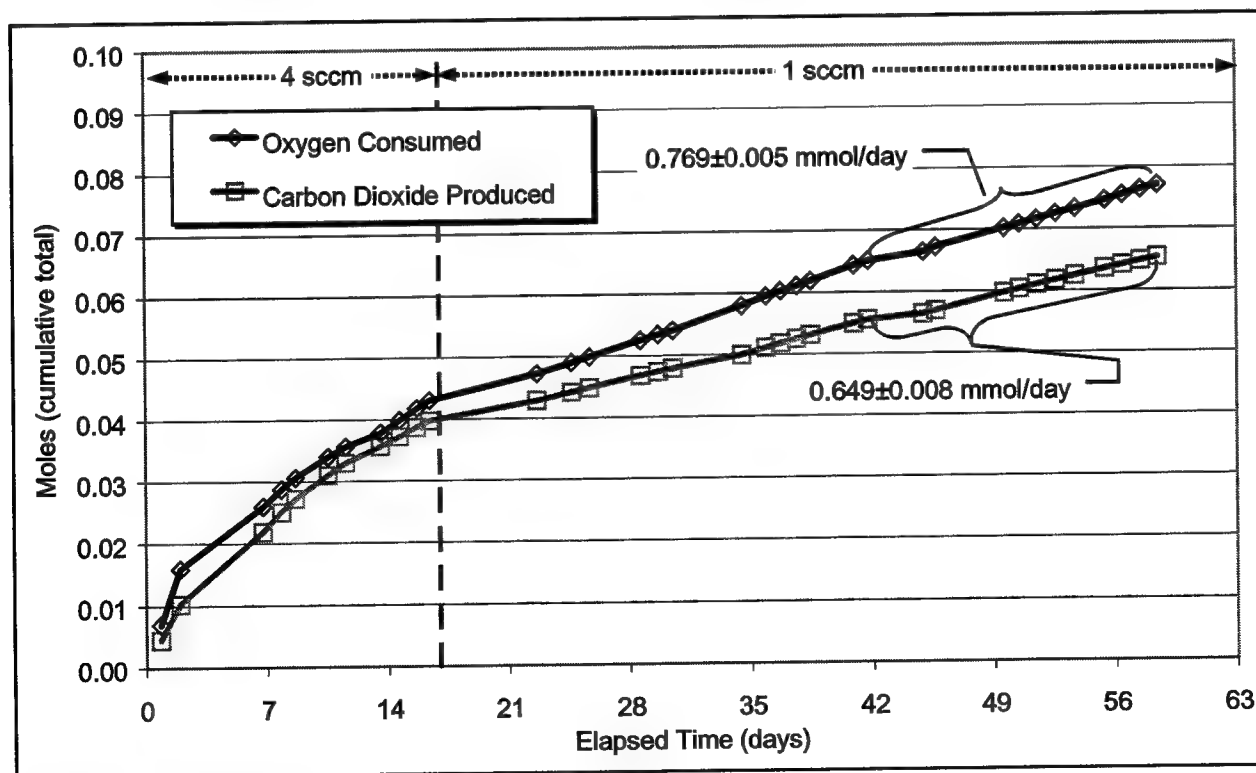


Figure 29. Cumulative O₂ consumption and CO₂ production vs time – biosparging

Figure 29, a steady rate of oxygen consumption and carbon dioxide production was reached and can be seen from day 42 to 58. From these data, a steady oxygen consumption rate of 0.77 mmole/day ($\sigma = 0.005$) and a steady carbon dioxide production rate of 0.65 mmole/day ($\sigma = 0.008$) was calculated. The estimated mass of contaminated soil in the column was 8.8 kg. The corresponding zero-order rate of hydrocarbon biological degradation from day 42 to 58 was 0.88-mg hydrocarbon kg contaminated soil⁻¹ day⁻¹.

A comparison of exit gas data (Figure 23) under the two different airflow rates appears to suggest a benefit from blowing air at a higher rate than the guidance given in the EPA Manual: Bioventing Principles and Practice. However, results from an identical evaluation of Area 1595 showed that the respiration rate decreased at approximately the same elapsed time in the evaluation. It is believed that the reduction of the respiration rate coinciding with the reduction of the airflow is a coincidence in this evaluation and that the respiration in the column would have settled at the same constant rate under both airflow rates. Evaluation of the oxygen content in the exit gas suggests that oxygen availability was never a limiting factor in the column for biological respiration. Therefore, we suggest that there is little benefit from blowing air at a higher rate than the EPA guidance.

The ratio of the carbon dioxide production rate and oxygen consumption rate is known as the respiration quotient (RQ). The characteristic value of RQ is dependent upon the nature of the substrate being metabolized by the cells. When carbohydrates are the substrate of interest, RQ values around 1.0 are generally observed under aerated conditions. Under the same conditions, metabolism of hydrocarbons yields RQ values around 0.67. For the bioventing column, an RQ value of 0.84 was observed suggesting hydrocarbon metabolism.

The calculated amount of rTPH degraded based on respiration data (2.46 g) accounts for less than half of the rTPH removal measured in the soil column (6.6 \pm 5.7 g). Based on this data and the lack of reliable analysis of VOCs in the exit gas, it is assumed that the remainder of the rTPH removed from the column was lost through volatilization. This suggests that volatilization was a very significant pathway for rTPH removal in the column than biodegradation. This result is not surprising given the volatility of the major compounds comprising unleaded gasoline.

Conclusions from Phase II

Based on the analysis of soil and aqueous phases, rTPH in this system was present predominantly in the soil phase. Significant removal of rTPH from the soil was observed under all three treatment conditions evaluated. rTPH losses from the bioventing and biosparging columns were much higher than that seen in the natural attenuation column. The estimated removal rate of rTPH contamination from the soil was 2.5-, 17.5-, and 12.9-mg rTPH kg contaminated soil⁻¹ day⁻¹ for natural attenuation, bioventing, and biosparging, respectively. These data suggest that remediation of the contamination site will proceed approximately six times faster with active aeration.

The rates of biodegradation in the cases of bioventing and biosparging were calculated from the exit gas analyses. These results suggest steady-state biodegradation rates of 0.27 and 0.88-mg rTPH kg contaminated soil⁻¹ day⁻¹ for bioventing and biosparging, respectively. These results suggest that biosparging of the contamination site will result in much higher levels of biological degradation than bioventing. Because the total rTPH degraded based on respiration data is a small fraction of the total rTPH reduction in the column, the data suggest that the most significant mode of rTPH removal was through volatilization. The ratio of rTPH removed by biodegradation to total rTPH removed from the column was three times higher under biosparging than bioventing. This suggests that biosparging may promote a higher biodegradation rate and reduce the rate of volatilization of rTPH from the soil due to aeration.

Because of the ability of the groundwater to transport the contaminant offsite, aqueous-phase rTPH contamination may be the area of most concern even though it represents only a small fraction of the total contamination at this site. Based on the aqueous-rTPH concentrations in the saturated zone, natural attenuation showed little or no removal of rTPH from the aqueous. This suggests that natural attenuation will not be effective in controlling rTPH migration in the groundwater. Both bioventing and biosparging showed significant removal of rTPH from the aqueous phase. The first-order removal rate constants for bioventing and biosparging were 2.65 and 1.82 day⁻¹, respectively. This suggests that active aeration of the site will assist in the attenuating the migration of rTPH in the groundwater.

Appendix A

Phase I Data

AREA 1795										
TPH and LIPID BIOMARKER RESULTS										
PLFA	core depth, ft			avg.		s.d.			avg.	
	0.5	0.5	0.5	0.5	0.5	2.0	2.0	2.0	2.0	2.0
TPH (ppm)	38	3	3	15	20	14	0	1	5	8
Biomass (pmol/g)	23,183	27,687	33,869	28,246	5,365	1,879	2,609	2,747	2,412	467
15:0	0.6	0.6	0.6	0.6	0.0	0.6	0.8	0.0	0.5	0.4
16:0	12.0	11.7	12.9	12.2	0.6	11.5	10.9	11.5	11.3	0.3
17:0	0.6	0.7	0.7	0.7	0.1	1.2	1.3	0.0	0.8	0.7
18:0	2.7	4.7	5.3	4.2	1.4	4.6	4.6	4.5	4.6	0.1
20:0	0.0	0.5	0.5	0.4	0.3	0.5	0.6	0.0	0.4	0.3
Normal saturates (ubiquitous)	15.9	18.3	20.0	18.0	2.1	18.4	18.3	16.0	17.6	1.3
i14:0	0.4	0.5	0.5	0.4	0.1	0.0	0.6	0.0	0.2	0.4
i15:0	5.4	5.8	5.7	5.6	0.2	3.1	3.8	4.0	3.6	0.5
a15:0	3.4	4.0	3.7	3.7	0.3	2.1	2.8	2.6	2.5	0.4
i16:0	3.1	3.0	2.8	3.0	0.1	3.0	2.7	2.9	2.9	0.1
i17:0	1.8	1.9	1.7	1.8	0.1	4.2	4.0	4.4	4.2	0.2
a17:0	3.3	3.1	2.7	3.0	0.3	3.4	2.5	2.7	2.8	0.5
Terminally branched saturates (Gram-positive)	17.3	18.3	17.2	17.6	0.6	15.8	16.5	16.5	16.3	0.4
16:1w9c	1.7	1.5	1.5	1.6	0.1	0.0	1.3	1.5	0.9	0.8
16:1w7c	8.2	6.5	6.1	7.0	1.1	4.7	3.9	4.5	4.4	0.4
16:1w7t	0.6	1.5	1.7	1.3	0.6	1.3	1.6	1.7	1.5	0.2
16:1w5c	3.4	3.1	3.0	3.2	0.2	2.5	2.1	2.4	2.4	0.2
cy17:0	3.2	3.5	3.1	3.3	0.2	4.1	3.6	4.0	3.9	0.3
18:1w9c	8.7	7.3	6.7	7.5	1.0	8.3	6.1	5.6	6.7	1.4
18:1w7c	14.1	13.1	12.6	13.2	0.8	7.2	5.4	4.9	5.8	1.2
18:1w7t	0.7	1.9	1.9	1.5	0.7	0.0	0.0	0.0	0.0	0.0
18:1w5c	1.4	1.9	1.6	1.7	0.2	0.6	0.0	0.0	0.2	0.3
cy19:0	5.3	6.0	5.5	5.6	0.3	11.5	8.9	10.2	10.2	1.3
Monounsaturates (Gram-negative)	47.4	46.4	43.6	45.8	1.9	40.3	33.0	34.8	36.0	3.8
i15:1	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
a15:1	0.2	0.0	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0
i17:1w7c	3.0	2.4	2.1	2.5	0.5	2.3	1.6	2.0	2.0	0.4
br19:1	1.1	0.9	0.8	0.9	0.1	2.6	1.9	1.7	2.1	0.5
Branched monounsaturates (SRB/IRB)	4.3	3.4	2.9	3.5	0.7	4.9	3.6	3.8	4.1	0.7
10me16:0	5.0	6.0	5.5	5.5	0.5	10.6	9.3	12.0	10.6	1.3
br17:0	0.9	0.9	0.8	0.8	0.1	0.0	8.6	8.2	5.6	4.8
10me18:0	2.1	2.1	1.9	2.1	0.1	4.6	3.5	4.1	4.1	0.6
Midchain branched saturates (Actinomycete)	8.0	9.0	8.2	8.4	0.5	15.2	21.4	24.3	20.3	4.7
18:2w6	7.2	4.6	8.1	6.6	1.8	5.4	7.3	4.6	5.8	1.4
Polyunsaturates (eukaryotes)	7.2	4.6	8.1	6.6	1.8	5.4	7.3	4.6	5.8	1.4
Date extracted	Mar-97	Apr-97	Apr-97			Mar-97	Apr-97	Apr-97		

AREA 1795										
TPH and LIPID BIOMARKER RESULTS										
	core depth, ft			avg.	s.d.	core depth, ft			avg.	s.d.
PLEA	4.5	4.5	4.5			7.0	7.0	7.0		
TPH (ppm)	2	1	0	1	1	10	1	0	4	6
Biomass (pmol/g)	428	275	391	365	80	588	459	437	494.7	81.7
15:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16:0	12.9	17.4	18.1	16.1	2.8	12.6	22.5	23.2	19.4	5.9
17:0	18.4	0.0	0.0	6.1	10.6	31.5	0.0	0.0	10.5	18.2
18:0	5.7	9.7	8.6	8.0	2.1	4.8	8.5	8.1	7.1	2.0
20:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Normal saturates	37.0	27.1	26.7	30.3	5.8	48.8	31.0	31.2	37.1	10.3
(ubiquitous)										
i14:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
i15:0	2.8	6.8	4.7	4.8	2.0	1.4	5.5	6.0	4.3	2.5
a15:0	6.2	0.0	0.0	2.1	3.6	6.3	3.6	0.0	3.3	3.1
i16:0	5.7	8.5	6.5	6.9	1.4	2.3	4.3	4.6	3.7	1.3
i17:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
a17:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Terminally branched saturates	14.8	15.3	11.2	13.8	2.2	10.0	13.4	10.7	11.3	1.8
(Gram-positive)										
16:1w9c	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16:1w7c	4.1	10.8	10.0	8.3	3.7	4.6	12.3	12.7	9.8	4.6
16:1w7t	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16:1w5c	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cy17:0	8.7	14.0	11.3	11.3	2.6	8.0	15.8	17.0	13.6	4.9
18:1w9c	4.0	0.0	5.8	3.3	3.0	4.0	0.0	0.0	1.3	2.3
18:1w7c	9.8	13.8	13.3	12.3	2.2	12.7	17.5	17.3	15.8	2.7
18:1w7t	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
18:1w5c	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cy19:0	12.3	19.1	13.8	15.0	3.6	6.3	10.0	11.2	9.2	2.5
Monounsaturates	39.0	57.6	54.1	50.2	9.9	35.5	55.6	58.1	49.7	12.4
(Gram-negative)										
i15:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
a15:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
i17:1w7c	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
br19:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Branched monounsaturates	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
(SRB/IRB)										
10me16:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
br17:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10me18:0	3.2	0.0	0.0	1.1	1.8	5.6	0.0	0.0	1.9	3.3
Midchain branched saturates	3.2	0.0	0.0	1.1	1.8	5.6	0.0	0.0	1.9	3.3
(Actinomycete)										
18:2w6	6.0	0.0	7.9	4.7	4.1	0.0	0.0	0.0	0.0	0.0
Polyunsaturates	6.0	0.0	7.9	4.7	4.1	0.0	0.0	0.0	0.0	0.0
(eukaryotes)										
Date extracted	Mar-97	Apr-97	Apr-97			Mar-97	Apr-97	Apr-97		

AREA 1795										
TPH and LIPID BIOMARKER RESULTS										
PLFA	core depth, ft			avg.	s.d.	core depth, ft			avg.	s.d.
	8.5	8.5	8.5			9.5	9.5	9.5		
TPH (ppm)	26	3	1	10	14	50	23	2	25	24
Biomass (pmol/g)	3,144	4,954	2,475	3,525	1,283	3,874	4,539	4,561	4,325	391
15:0	0.5	0.8	0.3	0.6	0.2	0.3	0.3	0.7	0.5	0.2
16:0	19.6	22.7	21.0	21.1	1.5	15.3	18.0	17.7	17.0	1.5
17:0	3.1	0.9	1.0	1.7	1.2	1.6	1.0	1.0	1.2	0.3
18:0	2.2	3.5	5.3	3.7	1.6	1.5	4.2	4.0	3.2	1.5
20:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Normal saturates (ubiquitous)	25.5	27.9	27.7	27.0	1.4	18.7	23.6	23.4	21.9	2.8
i14:0	0.5	1.0	0.0	0.5	0.5	0.0	0.0	0.0	0.0	0.0
i15:0	1.5	2.4	1.0	1.7	0.7	1.1	1.4	1.0	1.1	0.2
a15:0	2.5	3.1	1.4	2.3	0.8	0.8	0.7	0.6	0.7	0.1
i16:0	5.3	6.4	5.4	5.7	0.6	1.0	0.8	0.7	0.8	0.1
i17:0	0.5	0.5	0.5	0.5	0.0	1.0	1.0	1.0	1.0	0.0
a17:0	1.0	1.0	1.0	1.0	0.0	0.5	0.5	0.5	0.5	0.0
Terminally branched saturates (Gram-positive)	11.4	14.3	9.5	11.7	2.4	4.4	4.3	3.9	4.2	0.3
16:1w9c	1.1	0.0	0.7	0.6	0.6	0.6	0.6	0.0	0.4	0.4
16:1w7c	12.3	11.2	8.6	10.7	1.9	12.1	14.2	11.3	12.6	1.5
16:1w7t	2.2	3.3	2.8	2.8	0.5	1.7	0.7	3.1	1.8	1.2
16:1w5c	1.0	1.2	0.9	1.0	0.1	0.0	0.0	0.0	0.0	0.0
cy17:0	18.6	19.0	21.0	19.5	1.3	15.7	16.0	16.0	15.9	0.2
18:1w9c	1.4	1.5	1.3	1.4	0.1	0.6	0.0	0.0	0.2	0.4
18:1w7c	15.6	12.2	15.7	14.5	2.0	31.2	30.8	32.1	31.4	0.7
18:1w7t	1.9	2.2	2.6	2.2	0.3	4.0	0.7	0.7	1.8	1.9
18:1w5c	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cy19:0	6.2	5.1	7.6	6.3	1.3	9.0	8.8	9.0	8.8	0.2
Monounsaturates (Gram-negative)	60.2	55.6	61.3	59.0	3.0	75.0	71.5	72.1	72.9	1.9
i15:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
a15:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
i17:1w7c	0.3	0.4	0.0	0.2	0.2	0.4	0.0	0.0	0.1	0.2
br19:1	1.1	0.8	1.1	1.0	0.2	0.8	0.6	0.6	0.7	0.1
Branched monounsaturates (SRB/IRB)	1.5	1.1	1.1	1.2	0.2	1.1	0.6	0.6	0.8	0.3
10me16:0	0.0	0.4	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.0
br17:0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10me18:0	0.5	0.0	0.0	0.2	0.3	0.0	0.0	0.0	0.0	0.0
Midchain branched saturates (Actinomycete)	0.5	0.4	0.0	0.3	0.3	0.0	0.0	0.0	0.0	0.0
18:2w6	0.9	0.7	0.5	0.7	0.2	0.7	0.0	0.0	0.2	0.4
Polyunsaturates (eukaryotes)	0.9	0.7	0.5	0.7	0.2	0.7	0.0	0.0	0.2	0.4
Date extracted	Mar-97	Apr-97	Apr-97			Mar-97	Apr-97	Apr-97		

AREA 1795					
TPH and LIPID BIOMARKER RESULTS					
	core depth, ft			avg.	s.d.
PLFA	12.0	12.0	12.0		
TPH (ppm)	1,924	551	47	841	971
Biomass (pmol/g)	316	305	504	375	112
15:0	0.0	0.0	0.0	0.0	0.0
16:0	21.6	30.6	24.3	25.5	4.6
17:0	5.7	0.0	0.0	1.9	3.3
18:0	5.3	11.1	9.8	8.7	3.0
20:0	0.0	0.0	4.6	1.5	2.7
Normal saturates	32.6	41.7	38.7	37.6	4.6
(ubiquitous)					
i14:0	0.0	0.0	0.0	0.0	0.0
i15:0	0.0	0.0	2.0	0.7	1.1
a15:0	0.0	0.0	0.0	0.0	0.0
i16:0	0.0	0.0	0.0	0.0	0.0
i17:0	0.0	0.0	0.0	0.0	0.0
a17:0	0.0	0.0	0.0	0.0	0.0
Terminally branched saturates	0.0	0.0	2.0	0.7	1.1
(Gram-positive)					
16:1w9c	0.0	0.0	0.0	0.0	0.0
16:1w7c	12.2	12.7	11.3	12.1	0.7
16:1w7t	0.0	0.0	2.4	0.8	1.4
16:1w5c	0.0	0.0	6.0	2.0	3.5
cy17:0	11.4	9.9	7.6	9.6	1.9
18:1w9c	3.8	6.4	6.1	5.5	1.4
18:1w7c	28.2	24.8	18.2	23.7	5.1
18:1w7t	0.0	0.0	3.0	1.0	1.7
18:1w5c	0.0	0.0	0.0	0.0	0.0
cy19:0	7.1	4.6	4.7	5.4	1.4
Monounsaturates	62.7	58.3	59.3	60.1	2.3
(Gram-negative)					
i15:1	0.0	0.0	0.0	0.0	0.0
a15:1	0.0	0.0	0.0	0.0	0.0
i17:1w7c	0.0	0.0	0.0	0.0	0.0
br19:1	0.0	0.0	0.0	0.0	0.0
Branched monounsaturates	0.0	0.0	0.0	0.0	0.0
(SRB/IRB)					
10me16:0	0.0	0.0	0.0	0.0	0.0
br17:0	0.0	0.0	0.0	0.0	0.0
10me18:0	0.0	0.0	0.0	0.0	0.0
Midchain branched saturates	0.0	0.0	0.0	0.0	0.0
(Actinomycete)					
18:2w6	4.8	0.0	0.0	1.6	2.7
Polyunsaturates	4.8	0.0	0.0	1.6	2.7
(eukaryotes)					
Date extracted	Mar-97	Apr-97	Apr-97		

Acetate Microcosm $^{14}\text{CO}_2$ Data

Saturated (% $^{14}\text{CO}_2$ accumulation)

incubation time (hours)	Top of smear zone		Bottom of smear zone	
	avg.	s.d.	avg.	s.d.
2	0.02	0.01	0.05	0.01
4	0.06	0.01	0.18	0.01
7	0.14	0.01	0.35	0.01
10	0.18	0.01	0.45	0.01
15	0.23	0.01	0.56	0.01
20	0.28	0.01	0.66	0.01
23	0.30	0.01	0.72	0.01
48	0.36	0.01	0.75	0.01
60	0.43	0.01	0.78	0.01
72	0.49	0.01	0.81	0.01
84	0.52	0.01	0.85	0.01
96	0.55	0.01	0.88	0.01
108	0.56	0.01	0.90	0.01
120	0.57	0.01	0.91	0.01
132	0.58	0.01	0.93	0.01
144	0.59	0.01	0.93	0.01
168	0.59	0.01	0.93	0.01

Unsaturated (% $^{14}\text{CO}_2$ accumulation)

incubation time (hours)	Top of smear zone		Bottom of smear zone	
	avg.	s.d.	avg.	s.d.
0			0.00	0.00
4			0.45	0.35
8			0.75	0.23
12			1.40	0.55
24			1.69	0.25
32			2.06	0.25
48			2.42	0.25
56			2.60	0.11
68			2.83	0.15
80			3.04	0.16
92			3.20	0.11
116			3.33	0.07
140			3.62	0.12
164			3.81	0.12
188			4.07	0.13

Phenanthrene Microcosm $^{14}\text{CO}_2$ Data

Saturated (% $^{14}\text{CO}_2$ accumulation)

Top of the Smear Zone

Incubation time (days)	Sterile Control		Control		H ₂ O ₂ +nutrient		H ₂ O ₂		Nutrient	
	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.15	0.03	0.38	0.04	0.14	0.02	0.10	0.05	0.51	0.06
8	0.27	0.00	0.97	0.06	0.22	0.01	0.19	0.02	0.95	0.05
12	0.39	0.01	2.02	0.24	0.28	0.01	0.28	0.03	1.26	0.02
15	0.50	0.00	3.10	0.40	0.36	0.01	0.36	0.02	1.48	0.03
19	0.57	0.02	5.74	0.79	0.42	0.01	0.42	0.01	1.76	0.13
22	0.66	0.02	7.65	0.51	0.49	0.04	0.48	0.01	2.00	0.10
26	0.78	0.01	9.95	0.13	0.60	0.04	0.53	0.02	2.16	0.12
29	0.87	0.00	11.36	0.47	0.67	0.02	0.59	0.01	2.29	0.07
33	0.98	0.00	12.39	1.28	0.74	0.03	0.65	0.01	2.51	0.20
36	1.07	0.01	13.16	1.01	0.81	0.03	0.72	0.01	2.68	0.13
40	1.16	0.00	14.03	0.89	0.88	0.02	0.78	0.01	2.84	0.11
43	1.25	0.01	14.82	0.71	0.92	0.02	0.84	0.01	2.98	0.10
47	1.32	0.01	15.73	0.64	1.00	0.02	0.89	0.01	3.12	0.08

Unsaturated (% $^{14}\text{CO}_2$ accumulation)

Top of the Smear Zone

Incubation time (days)	Sterile Control		Control		H ₂ O ₂ +nutrient		H ₂ O ₂		Nutrient	
	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.
2	0.11	0.01	0.25	0.01	0.07	0.01	0.08	0.03	0.14	0.02
6	0.37	0.05	1.21	0.42	0.17	0.01	0.24	0.07	0.27	0.03
9	0.40	0.01	1.71	0.18	0.19	0.01	0.29	0.03	0.30	0.01
13	0.54	0.01	2.25	0.34	0.26	0.01	0.37	0.02	0.37	0.02
15	0.65	0.01	2.74	0.26	0.31	0.01	0.45	0.02	0.42	0.01
19	0.83	0.01	3.40	0.24	0.40	0.02	0.57	0.03	0.52	0.02
22	0.92	0.01	3.75	0.06	0.46	0.01	0.64	0.03	0.58	0.00
26	1.00	0.02	4.42	0.34	0.51	0.01	0.72	0.03	0.64	0.02
29	1.10	0.00	4.89	0.22	0.57	0.01	0.79	0.01	0.70	0.01
33	1.21	0.01	5.50	0.42	0.64	0.01	0.88	0.04	0.77	0.02
36	1.30	0.01	5.95	0.31	0.68	0.01	0.93	0.02	0.82	0.02
40	1.36	0.03	6.48	0.46	0.75	0.02	0.98	0.01	0.85	0.01
43	1.41	0.01	6.89	0.36	0.76	0.01	1.01	0.01	0.87	0.01
47	1.49	0.01	7.31	0.32	0.81	0.01	1.06	0.02	0.92	0.01

Phenanthrene Microcosm ¹⁴CO₂ Data

Saturated (% ¹⁴CO₂ accumulation)

Bottom of the smear zone

Incubation time (days)	Sterile Control		Control		H ₂ O ₂ +nutrient		H ₂ O ₂		Nutrient	
	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	0.16	0.01	0.31	0.00	0.20	0.12	0.11	0.03	0.44	0.00
8	0.30	0.01	0.75	0.03	0.31	0.10	0.22	0.05	0.82	0.00
12	0.44	0.00	1.40	0.10	0.47	0.15	0.35	0.06	1.11	0.00
15	0.57	0.01	1.63	0.10	0.57	0.14	0.47	0.08	1.75	0.00
19	0.69	0.02	3.04	0.14	0.67	0.14	0.54	0.11	2.05	0.00
22	0.78	0.02	4.28	0.22	0.75	0.14	0.63	0.14	2.31	0.00
26	0.90	0.02	6.01	0.42	0.84	0.15	0.74	0.18	2.78	0.00
29	1.00	0.02	6.97	0.54	0.92	0.16	0.82	0.20	3.08	0.00
33	1.12	0.02	7.64	0.57	1.01	0.18	0.92	0.24	3.38	0.00
36	1.22	0.03	8.17	0.85	1.08	0.19	1.12	0.22	3.68	0.00
40	1.33	0.03	8.59	1.28	1.16	0.19	1.21	0.26	3.87	0.00
43	1.43	0.04	8.93	1.63	1.23	0.20	1.29	0.29	3.99	0.00
47	1.53	0.04	9.41	2.15	1.29	0.20	1.37	0.32	4.10	0.00

Unsaturated (% ¹⁴CO₂ accumulation)

Bottom of the smear zone

Incubation time (days)	Sterile Control		Control		H ₂ O ₂ +nutrient		H ₂ O ₂		Nutrient	
	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.	avg.	s.d.
2	0.12	0.02	0.39	0.03	0.15	0.03	0.15	0.07	0.16	0.04
6	0.38	0.02	0.89	0.06	0.29	0.02	0.36	0.05	0.31	0.03
9	0.42	0.01	1.01	0.03	0.33	0.03	0.43	0.03	0.34	0.01
13	0.59	0.01	1.17	0.02	0.42	0.02	0.56	0.02	0.45	0.01
15	0.71	0.01	1.28	0.01	0.49	0.01	0.65	0.01	0.52	0.01
19	0.91	0.01	1.45	0.01	0.60	0.01	0.78	0.01	0.66	0.01
22	1.02	0.03	1.53	0.01	0.67	0.01	0.85	0.01	0.73	0.00
26	1.16	0.03	1.63	0.01	0.74	0.01	0.95	0.03	0.82	0.02
29	1.27	0.01	1.73	0.02	0.80	0.00	1.03	0.01	0.90	0.01
33	1.41	0.01	1.83	0.01	0.89	0.01	1.13	0.01	1.00	0.01
36	1.49	0.02	1.90	0.01	0.95	0.01	1.20	0.01	1.08	0.01
40	1.60	0.04	1.95	0.02	1.00	0.02	1.28	0.03	1.12	0.01
43	1.63	0.01	1.99	0.01	1.02	0.01	1.31	0.01	1.16	0.01
47	1.73	0.01	2.05	0.01	1.09	0.01	1.38	0.01	1.24	0.01

Appendix B

Phase II Natural Attenuation

Data

Fort Drum Area 1795, Natural Attenuation

Location	Date Elapsed Time (days)	1 Sep 0	3 Sep 2	18 Sep 17	2 Oct 31	14 Oct 43	30 Oct 59
Column	H ₂ O added (mL)	585	585	585	585	700	700
	TPH (µg/mL)	5.513	5.513	5.513	5.513	5.513	5.513
	TPH added (µg)	3,225	3,225	3,225	3,225	3,859	3,859
	TPH in air (ng/scm)						
	Flow rate (scm/min)						
	Start						
	End						
N1-0	Duration (days)						
	TPH Volatilized (µg)						
	H ₂ O withdrawn (mL)	215	215	215	215	215	215
	TPH (µg/mL)	0.317	0.472	0.793	1.621	1.804	0.661
	TPH withdrawn (µg)	68	101	170	348	388	142
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	2	0	0	0	0	0
N1-10	Total rTPH (µg)	2,081	0	0	0	0	0
	H ₂ O withdrawn (mL)	215	215	215	215	215	215
	TPH (µg/mL)	1.580	0.158	2.044	1.177	1.558	0.777
	TPH withdrawn (µg)	340	34	439	253	335	167
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	5,721	0	0	0	0	0
N1-23	H ₂ O withdrawn (mL)	80	80	80	80	180	180
	TPH (µg/mL)	1.814	0.208	1.959	0.500	5.470	6.328
	TPH withdrawn (µg)	145	17	157	40	985	1139
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	88	48	22	9	12	103
	Total rTPH (µg)	229,367	125,578	56,309	23,469	30,580	270,384
	Soil (g)	2617	2617	2617	2617	2617	2617
N1-34	rTPH (µg/g)	456	490	890	469	136	312
	Total rTPH (µg)	1,193,388	1,283,368	2,330,232	1,226,739	354,988	816,310
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1026	1627	295	55	563	807
	Total rTPH (µg)	2,686,753	4,258,663	772,862	144,848	1,474,117	2,111,536
	Soil (g)	1974	2638	2638	2638	2638	1974
	rTPH (µg/g)	310	28	31	4	2	2
N1-58	Total rTPH (µg)	611,171	73,810	81,841	10,823	4,247	4,006
	Soil (g)	665	0	0	0	0	665
	rTPH (µg/g)	4	0	0	0	0	1
	Total rTPH (µg)	2,391	0	0	0	0	569
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	25	0	0	0	0	0
	Total rTPH (µg)	27,664	0	0	0	0	0
N2-0	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,889	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	2,892	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
N2-10	rTPH (µg/g)	3	0	0	0	0	0
	Total rTPH (µg)	7,717	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	2,232	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
	rTPH (µg/g)	1	0	0	0	0	0
N2-23	Total rTPH (µg)	1,151	0	0	0	0	0
	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	1,610	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,151	0	0	0	0	0
N2-34	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	2,232	0	0	0	0	0
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	2,232	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
N2-46	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,151	0	0	0	0	0
	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	1,610	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
	rTPH (µg/g)	1	0	0	0	0	0
N2-58	Total rTPH (µg)	1,151	0	0	0	0	0
	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	1,610	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,151	0	0	0	0	0
N2-TOP	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	1,610	0	0	0	0	0
	Soil (g)	2129	3126	3126	3126	3126	2129
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,151	0	0	0	0	0
	Soil (g)	997	0	0	0	0	997
rTPH (µg) on soil		4,776,027	5,741,418	3,241,244	1,405,879	1,863,932	3,202,806

		Area 1795 Natural Attenuation						
LOCATION	Date	29 Aug	1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
	Time (days)	0	0	2	17	31	43	59
	2-Top	2						0
	2-58	1						0
	2-46	1						0
	2-34	3						0
	2-23	1						0
	2-10	1						0
	2-0	25						0
	1-TOP	4						1
	1-58	310		28	31	4	2	2
	1-46	1026		1627	295	55	563	807
	1-34	456		490	890	469	136	312
	1-23	88		48	22	9	12	103
	1-10	2		0	0	0	0	0
	1-0	2						0

rTPH on soil in mg/kg

blank=no sample or not analyzed

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	611	0	0	0	0	611
2-58	1305	1917	1917	1917	1917	1305
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	669	0	0	0	0	669
1-TOP	408	0	0	0	0	408
1-58	1210	1618	1618	1618	1618	1210
1-46	1605	1605	1605	1605	1605	1605
1-34	1605	1605	1605	1605	1605	1605
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	17710	17710	17710	17710	17710	17710

$$\gamma_d \text{ (kN/m}^3\text{)} = 16$$

$$\gamma_d \text{ (g/cm}^3\text{)} = 1.63$$

$$\text{Column I.D. (in.)} = 3.25$$

$$\text{Column I.D. (cm)} = 8.26$$

$$\text{X-section (cm}^2\text{)} = 53.5$$

Contaminated Soil

$$\text{Estimated mass of soil} = 28,885 \text{ g}$$

$$\text{Estimated mass of contaminated soil} = 10,916 \text{ g}$$

Indicates both yellow and red described above

		Area 1795 Natural Attenuation					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	4.56E+07					3.15E+07
	2-58	2.06E+07					4.08E+05
	2-46	2.92E+06					4.69E+04
	2-34	5.22E+07					3.89E+07
	2-23	4.37E+07					2.13E+07
	2-10	2.40E+06					0.00E+00
	2-0	3.90E+06					1.91E+06
	1-TOP	4.35E+06					5.04E+06
	1-58	1.66E+07					1.74E+07
	1-46	1.16E+08					7.40E+07
	1-34	1.38E+07					1.67E+08
	1-23	7.83E+06					1.10E+08
	1-10	4.23E+06					1.07E+07
	1-0	3.83E+06					1.86E+07

Biomass (cells/g) 3.38E+08

4.97E+08

blank=no sample
or not analyzed

		Area 1795 Natural Attenuation					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	1.82E+03					1.26E+03
	2-58	8.25E+02					1.63E+01
	2-46	1.17E+02					1.87E+00
	2-34	2.09E+03					1.56E+03
	2-23	1.75E+03					8.52E+02
	2-10	9.60E+01					0.00E+00
	2-0						
	1-TOP	1.74E+02					2.02E+02
	1-58	6.63E+02					6.96E+02
	1-46	4.63E+03					2.96E+03
	1-34	5.53E+02					6.67E+03
	1-23	3.13E+02					4.41E+03
	1-10	1.69E+02					4.26E+02
	1-0	1.53E+02					7.43E+02

PLFA in soil (pmole/g)

1.34E+04

1.98E+04

~ 25,000 cells/
pmole PLFA

Appendix C

Phase II Bioventing Data

Fort Drum Area 1795, Bioventing

Location	Date	1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
	Elapsed Time (days)	0	2	17	31	43	59
Column	H ₂ O added (mL)	570	570	570	570	680	680
	TPH (µg/mL)	5.513	5.513	5.513	5.513	5.513	5.513
	TPH added (µg)	3142	3142	3142	3142	3749	3749
	TPH in air (ng/sccm)		13.8	13.8	13.8	13.8	13.8
	Flow rate (sccm/min)		4	1	1	1	1
	Start		9/1/97 22:15	9/4/97 23:00	9/20/97 14:10	10/3/97 12:45	10/15/97 12:40
	End		9/3/97 22:00	9/18/97 8:00	10/2/97 10:00	10/13/97 15:53	10/30/97 10:00
	Duration (days)		1.99	13.38	11.83	10.13	14.89
V1-0	TPH Volatilized (µg)		153	286	235	201	296
	H ₂ O withdrawn (mL)	214	214	214	214	220	220
	TPH (µg/mL)	1.351	2.419	2.708	1.155	1.836	1.469
	TPH withdrawn (µg)	289	518	579	247	404	323
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,190	0	0	0	0	0
V1-10	H ₂ O withdrawn (mL)	200	200	200	200	220	220
	TPH (µg/mL)	0.207	0.725	1.392	0.762	1.338	0.477
	TPH withdrawn (µg)	41	145	278	152	294	105
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	12	18	0	0	0	0
	Total rTPH (µg)	31,881	66,456	0	0	0	0
V1-23	H ₂ O withdrawn (mL)	86	86	86	86	150	150
	TPH (µg/mL)	10.813	2.336	5.710	1.677	0.555	0.463
	TPH withdrawn (µg)	930	201	491	144	83	70
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	7819	5125	3019	545	1360	4388
	Total rTPH (µg)	20,465,368	13,415,358	7,903,257	1,687,368	3,560,215	11,485,355
V1-34	Soil (g)	2399	2399	2399	2399	2399	2399
	rTPH (µg/g)	2316	487	500	456	73	293
	Total rTPH (µg)	5,556,279	1,167,541	1,198,792	1,094,445	175,180	701,861
V1-46	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	3	0	0	0	1
	Total rTPH (µg)	3,773	8,340	0	0	1,306	1,507
V1-58	Soil (g)	2306	3303	3303	3303	3303	2306
	rTPH (µg/g)	39	12	10	7	2	18
	Total rTPH (µg)	89,840	40,805	34,251	24,075	7,036	42,542
V1-TOP	Soil (g)	2088	0	0	0	0	997
	rTPH (µg/g)	410	0	0	0	0	2
	Total rTPH (µg)	856,859	0	0	0	0	1,652
V2-0	Soil (g)	0	0	0	0	0	1091
	rTPH (µg/g)	0	0	0	0	0	77
	Total rTPH (µg)	0	0	0	0	0	83,479
V2-10	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	42	0	0	0	0	1
	Total rTPH (µg)	109,273	0	0	0	0	2,230
V2-23	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	2	0	0	0	0	2
	Total rTPH (µg)	4,323	0	0	0	0	5,377
V2-34	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	4,289	0	0	0	0	0
V2-46	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,540	0	0	0	0	0
V2-58	Soil (g)	2306	3303	3303	3303	3303	2306
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,700	0	0	0	0	0
V2-TOP	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	3	0	0	0	0	0
	Total rTPH (µg)	3,337	0	0	0	0	0
rTPH (µg) on soil		27,129,652	14,698,500	9,136,300	2,805,888	3,743,737	12,324,002
TPH degraded (µg) based on respiration data				301,075	93,442	62,440	69,284

		Area 1795 Bioventing						
LOCATION	Date	29 Aug	1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
	Time (days)	0	0	2	17	31	43	59
	2-Top	3						0
	2-58	1						0
	2-46	1						0
	2-34	2						0
	2-23	2						2
	2-10	42						1
	2-0							77
	1-TOP	410						2
	1-58	39		12	10	7	2	18
	1-46	1		3	0	0	0	1
	1-34	2316		487	500	456	73	293
	1-23	7819		5125	3019	645	1360	4388
	1-10	12		18	0	0	0	0
	1-0	1						0

rTPH on soil in
mg/kg

blank=no sample
or not analyzed

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	611	0	0	0	0	611
2-58	1414	2025	2025	2025	2025	1414
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	0	0	0	0	0	669
1-TOP	1280	0	0	0	0	611
1-58	1414	2025	2025	2025	2025	1414
1-46	1605	1605	1605	1605	1605	1605
1-34	1471	1471	1471	1471	1471	1471
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	18093	18093	18093	18093	18093	18093

$$\gamma_d \text{ (kN/m}^3\text{)} = 16$$

$$\gamma_d \text{ (g/cm}^3\text{)} = 1.63$$

Column I.D. (in.) = 3.25
Column I.D. (cm) = 8.26
X-section (cm²) = 53.5

Contaminated Soil

Estimated mass of soil = 29,509 g
Estimated mass of contaminated soil = 14,645 g

semivolatile (mg/L)
Indicates that the detected level is below
the reporting limit but above the 99%
confidence detection limit

1785 Blowing				Tank		1785 Blowing					
Sample Start	Sample End	Elapsed Time (days)	Plotted Time of Sample (days)	Flow Rate @ Inlet (scfm)	O ₂ Sample (% by Vol.)	CO ₂ Sample (% by Vol.)	O ₂ Sample (% by Vol.)	ΔO ₂ (% by Vol.)	O ₂ (mol) Consumed	CO ₂ (mol) Produced	ΔCO ₂ (% by Vol.)
9/1/97 22:15	9/2/97 19:00	0.9	0.4	4	20.95%	0.04%	20.11%	0.83%	0.0175	0.0175	0.84%
9/2/97 19:00	9/3/97 22:00	2.0	1.4	4	20.95%	0.04%	20.63%	0.32%	0.0006	0.0181	0.52%
9/4/97 23:00	9/6/97 18:30	6.8	3.9	4	20.94%	0.03%	20.57%	0.54%	0.0029	0.0210	0.45%
9/6/97 18:30	9/9/97 18:15	7.8	7.3	4	20.95%	0.03%	20.43%	0.57%	0.0017	0.0226	0.47%
9/9/97 18:15	9/10/97 14:00	8.7	8.2	4	20.97%	0.04%	20.36%	0.55%	0.0032	0.0258	0.45%
9/10/97 14:00	9/12/97 11:45	10.6	9.6	4	21.14%	0.03%	20.30%	0.62%	0.0019	0.0277	0.47%
9/12/97 11:45	9/13/97 12:20	11.6	11.1	4	20.94%	0.03%	20.43%	0.51%	0.0015	0.0292	0.43%
9/13/97 12:20	9/15/97 12:00	13.6	12.6	4	20.92%	0.03%	20.50%	0.45%	0.0009	0.0301	0.40%
9/15/97 12:00	9/16/97 14:00	14.7	14.1	4	20.94%	0.04%	19.60%	1.20%	0.0018	0.0361	0.76%
9/16/97 14:00	9/17/97 8:00	16.7	15.2	4	20.95%	0.04%	20.10%	0.85%	0.0006	0.0367	0.71%
9/17/97 8:00	9/18/97 8:00	16.4	16.0	4	20.97%	0.03%	20.18%	0.81%	0.0017	0.0395	0.62%
9/18/97 8:00	9/24/97 14:00	22.7	18.8	1	20.80%	0.03%	20.25%	0.75%	0.0005	0.0390	0.60%
9/24/97 14:00	9/26/97 14:00	24.7	23.7	1	20.96%	0.04%	20.34%	0.76%	0.0005	0.0395	0.55%
9/26/97 14:00	9/27/97 15:15	25.7	25.2	1	20.95%	0.03%	19.82%	1.13%	0.0028	0.0423	0.67%
9/27/97 15:15	9/30/97 14:00	28.7	27.2	1	21.00%	0.04%	20.17%	0.78%	0.0008	0.0430	0.70%
9/30/97 14:00	10/1/97 14:00	29.7	29.2	1	20.95%	0.04%	20.31%	0.64%	0.0004	0.0434	0.61%
10/1/97 14:00	10/2/97 10:00	30.5	30.1	1	20.95%	0.03%	20.29%	0.67%	0.0004	0.0439	0.55%
10/2/97 10:00	10/6/97 10:00	34.5	32.2	1	20.95%	0.04%	20.29%	0.66%	0.0004	0.0442	0.53%
10/6/97 10:00	10/7/97 20:00	35.9	35.2	1	20.95%	0.04%	20.33%	0.63%	0.0011	0.0457	0.50%
10/7/97 20:00	10/9/97 14:30	36.7	36.3	1	20.95%	0.03%	19.76%	1.19%	0.0012	0.0469	0.62%
10/9/97 14:30	10/10/97 9:40	38.5	38.1	1	20.96%	0.03%	19.86%	1.06%	0.0006	0.0475	0.58%
10/10/97 9:40	10/12/97 20:00	40.9	39.7	1	20.92%	0.04%	20.37%	0.58%	0.0017	0.0491	0.52%
10/12/97 20:00	10/13/97 15:53	41.7	41.3	1	20.95%	0.03%	20.44%	0.51%	0.0004	0.0495	0.49%
10/13/97 15:53	10/16/97 20:30	44.9	42.4	1	20.95%	0.04%	20.37%	0.58%	0.0004	0.0499	0.51%
10/16/97 20:30	10/17/97 14:00	46.7	45.3	1	20.95%	0.03%	20.37%	0.57%	0.0004	0.0503	0.47%
10/17/97 14:00	10/21/97 13:00	49.6	47.6	1	20.94%	0.03%	20.37%	0.58%	0.0005	0.0508	0.45%
10/21/97 13:00	10/22/97 10:12	50.6	50.1	1	20.95%	0.03%	20.41%	0.58%	0.0007	0.0515	0.48%
10/22/97 10:12	10/23/97 11:00	51.5	51.0	1	20.95%	0.03%	20.39%	0.56%	0.0004	0.0519	0.45%
10/23/97 11:00	10/24/97 13:25	52.6	52.1	1	20.95%	0.03%	20.37%	0.58%	0.0004	0.0523	0.44%
10/24/97 13:25	10/26/97 16:00	53.7	53.2	1	20.95%	0.03%	20.37%	0.58%	0.0003	0.0526	0.43%
10/26/97 16:00	10/27/97 9:00	55.4	54.6	1	20.99%	0.03%	20.37%	0.58%	0.0003	0.0526	0.43%
10/27/97 9:00	10/28/97 9:15	56.5	56.0	1	20.95%	0.03%	20.37%	0.58%	0.0003	0.0526	0.43%
10/28/97 9:15	10/29/97 10:00	57.5	57.0	1	20.95%	0.03%	20.37%	0.58%	0.0003	0.0526	0.43%
10/29/97 10:00	10/30/97 9:00	58.4	58.0	1	20.95%	0.04%	20.37%	0.58%	0.0003	0.0526	0.43%

All sample measurements made @ 10°C and 1 atmosphere.

Linear estimation of cumulative O₂ consumption from day 42 to 61

O₂ consumption rate (moles/day) = 0.000404
 standard error of slope = 0.000002
 coefficient of determination = 1.000
 F statistic = 26108
 regression sum of squares = 0.000023

Linear estimation of cumulative CO₂ consumption from day 42 to 61

CO₂ consumption rate (moles/day) = 0.000319
 standard error of slope = 0.000004
 coefficient of determination = 0.999
 F statistic = 6303
 regression sum of squares = 0.000014

		Area 1795 Bioventing					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	4.74E+08					2.80E+08
	2-58	8.87E+07					4.35E+07
	2-46	2.00E+07					2.20E+07
	2-34	1.56E+06					8.06E+07
	2-23	3.32E+07					1.68E+08
	2-10	3.85E+06					9.99E+06
	2-0						2.06E+07
	1-TOP	8.10E+06					5.35E+07
	1-58	2.21E+07					3.56E+07
	1-46	2.61E+08					4.34E+07
	1-34	3.99E+07					8.47E+07
	1-23	7.58E+06					3.96E+07
	1-10	0.00E+00					1.49E+07
	1-0	2.00E+07					4.43E+07
Biomass (cells/g)		9.80E+08					9.41E+08

blank=no sample
or not analyzed

		Area 1795 Venting					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	1.89E+04					1.12E+04
	2-58	3.55E+03					1.74E+03
	2-46	7.99E+02					8.80E+02
	2-34	6.24E+01					3.22E+03
	2-23	1.33E+03					6.70E+03
	2-10	1.54E+02					3.99E+02
	2-0						
	1-TOP	3.24E+02					2.14E+03
	1-58	8.85E+02					1.42E+03
	1-46	1.04E+04					1.74E+03
	1-34	1.60E+03					3.39E+03
	1-23	3.03E+02					1.59E+03
	1-10	0.00E+00					5.96E+02
	1-0	8.00E+02					1.77E+03
PLFA in soil (pmole/g)		3.92E+04					3.68E+04

~ 25,000 cells/
pmole PLFA

Appendix D

Phase II Biosparging Data

Fort Drum Area 1795, Biosparging

Location	Date Elapsed Time (days)	1 Sep 0	3 Sep 2	18 Sep 17	2 Oct 31	14 Oct 43	30 Oct 59
Column	H ₂ O added (mL)	400	400	400	400	500	500
	TPH (µg/mL)	5.513	5.513	5.513	5.513	5.513	5.513
	TPH added (µg)	2205	2205	2205	2205	2756	2756
	TPH in air (ng/sccm)		830	830	830	830	830
	Flow rate (sccm/min)		4	1	1	1	1
	Start		9/1/97 22:15	9/4/97 23:00	9/20/97 14:10	10/3/97 12:45	10/15/97 12:40
	End		9/3/97 22:00	9/18/97 8:00	10/2/97 10:00	10/13/97 15:53	10/30/97 10:00
	Duration (days)		1.99	13.38	11.83	10.13	14.89
S1-0	TPH Volatilized (µg)		9,512	15,986	14,135	12,109	17,796
	H ₂ O withdrawn (mL)	200	200	200	200	200	200
	TPH (µg/mL)	1.135	0.000	0.506	0.285	0.452	0.280
	TPH withdrawn (µg)	227	0	101	57	90	56
	Soil (g)	1091	0	0	0	0	1091
	rTPH (µg/g)	12	0	0	0	0	0
	Total rTPH (µg)	13,432	0	0	0	0	0
S1-10	H ₂ O withdrawn (mL)	80	80	80	80	100	100
	TPH (µg/mL)	0.59	0.00	1.06	0.97	0.60	0.49
	TPH withdrawn (µg)	47	0	84	78	60	49
	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	4	0	0	0	0	0
	Total rTPH (µg)	11,217	0	0	0	0	0
S1-23	H ₂ O withdrawn (mL)	60	60	60	60	130	130
	TPH (µg/mL)	13.062	0.000	2.415	3.627	2.875	5.589
	TPH withdrawn (µg)	784	0	145	218	374	727
	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	4143	1826	3864	1807	2290	1907
	Total rTPH (µg)	10,844,493	4,780,461	10,114,642	4,729,694	5,993,403	4,991,770
S1-34	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1476	239	145	99	220	1277
	Total rTPH (µg)	3,864,568	626,642	379,281	259,135	574,903	3,342,975
S1-46	Soil (g)	1291	1291	1291	1291	1291	1291
	rTPH (µg/g)	145	0	22	3	0	4
	Total rTPH (µg)	187,292	0	28,833	3,800	361	5,392
S1-58	Soil (g)	2306	3303	3303	3303	3303	2306
	rTPH (µg/g)	9	10	10	7	1	24
	Total rTPH (µg)	20,794	34,449	31,688	21,876	2,264	54,867
S1-TOP	Soil (g)	2088	0	0	0	0	997
	rTPH (µg/g)	2	0	0	0	0	0
	Total rTPH (µg)	4,164	0	0	0	0	0
S2-0	Soil (g)	0	0	0	0	0	1091
	rTPH (µg/g)	0	0	0	0	0	0
	Total rTPH (µg)	0	0	0	0	0	0
S2-10	Soil (g)	2617	3708	3708	3708	3708	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,657	0	0	0	0	0
S2-23	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,795	0	0	0	0	0
S2-34	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	3,276	0	0	0	0	0
S2-46	Soil (g)	2617	2617	2617	2617	2617	2617
	rTPH (µg/g)	1	0	0	0	0	0
	Total rTPH (µg)	1,388	0	0	0	0	0
S2-58	Soil (g)	2306	3303	3303	3303	3303	2306
	rTPH (µg/g)	9	0	0	0	0	0
	Total rTPH (µg)	21,105	0	0	0	0	0
S2-TOP	Soil (g)	997	0	0	0	0	997
	rTPH (µg/g)	4	0	0	0	0	0
	Total rTPH (µg)	4,302	0	0	0	0	0
rTPH (µg) on soil		14,979,482	5,441,552	10,554,445	5,014,507	6,570,931	8,395,005
TPH degraded (µg) based on respiration data			159,193	271,565	110,217	109,518	119,570

LOCATION	Date Time (days)	Area 1795 Biosparging						
		29 Aug	1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
		0	0	2	17	31	43	59
	2-Top	4						0
	2-58	9						0
	2-46	1						0
	2-34	1						0
	2-23	1						0
	2-10	1						0
	2-0							0
	1-TOP	2						0
	1-58	9		10	10	7	1	24
	1-46	145		0	22	3	0	4
	1-34	1476		239	145	98	220	1277
	1-23	4143		1826	3864	1807	2290	1907
	1-10	4		0	0	0	0	0
	1-0	12						0

rTPH on soil in
mg/kg

blank=no sample
or not analyzed

Column-Port	Estimated soil volume attributed to sample (cm ³)					
2-TOP	611	0	0	0	0	611
2-58	1414	2025	2025	2025	2025	1414
2-46	1605	1605	1605	1605	1605	1605
2-34	1605	1605	1605	1605	1605	1605
2-23	1605	1605	1605	1605	1605	1605
2-10	1605	2273	2273	2273	2273	1605
2-0	0	0	0	0	0	669
1-TOP	1280	0	0	0	0	611
1-58	1414	2025	2025	2025	2025	1414
1-46	792	792	792	792	792	792
1-34	1605	1605	1605	1605	1605	1605
1-23	1605	1605	1605	1605	1605	1605
1-10	1605	2273	2273	2273	2273	1605
1-0	669	0	0	0	0	669
	17413	17413	17413	17413	17413	17413

$$\gamma_d \text{ (kN/m}^3\text{)} = 16$$

$$\gamma_d \text{ (g/cm}^3\text{)} = 1.63$$

Column I.D. (in.) = 3.25

Column I.D. (cm) = 8.26

X-section (cm²) = 53.5

Contaminated Soil

Estimated mass of soil = 28,401 g

Estimated mass of contaminated soil = 8,832 g

D4

1705 Biosparging													
Tank		Cumulative											
O ₂ Sample (% by Vol.)	CO ₂ Sample (% by Vol.)	O ₂ Sample (% by Vol.)	ΔO ₂ (% by Vol.)	O ₂ (mol) Consumed	O ₂ (mol) Consumed	CO ₂ Sample (% by Vol.)	ΔCO ₂ (% by Vol.)	CO ₂ (mol) Produced	CO ₂ (mol) Produced				
18.19%	0.04%	19.92%	1.03%	0.0069	0.0069	1.94%	1.90%	0.0045	0.0045				
20.95%	0.04%	19.96%	0.98%	0.0101	0.0159	1.19%	1.15%	0.0058	0.0103				
20.95%	0.02%	20.08%	0.87%	0.0028	0.0288	1.11%	1.09%	0.0032	0.0251				
20.95%	0.03%	20.30%	0.67%	0.0034	0.0340	0.77%	0.74%	0.0038	0.0310				
21.14%	0.04%	20.53%	0.61%	0.0016	0.0356	0.74%	0.70%	0.0020	0.0330				
20.94%	0.03%	20.51%	0.43%	0.0022	0.0379	0.53%	0.50%	0.0027	0.0357				
20.92%	0.03%	20.28%	0.68%	0.0020	0.0399	0.56%	0.53%	0.0015	0.0372				
20.94%	0.03%	20.27%	0.67%	0.0019	0.0418	0.58%	0.55%	0.0015	0.0387				
20.95%	0.04%	20.34%	0.61%	0.0012	0.0431	0.57%	0.53%	0.0011	0.0398				
20.92%	0.04%	19.56%	1.24%	0.0042	0.0473	1.01%	0.98%	0.0032	0.0430				
20.80%	0.03%	19.79%	1.17%	0.0018	0.0491	0.97%	0.94%	0.0013	0.0443				
20.96%	0.04%	19.77%	1.22%	0.0026	0.0525	0.97%	0.94%	0.0019	0.0468				
21.00%	0.04%	19.78%	1.22%	0.0009	0.0534	0.97%	0.93%	0.0006	0.0475				
21.10%	0.05%	19.93%	1.17%	0.0007	0.0541	0.91%	0.87%	0.0005	0.0479				
20.95%	0.03%	19.41%	1.54%	0.0039	0.0580	0.95%	0.91%	0.0021	0.0500				
20.95%	0.04%	19.44%	1.51%	0.0015	0.0595	1.22%	1.18%	0.0011	0.0512				
20.96%	0.03%	19.66%	1.37%	0.0008	0.0603	1.23%	1.19%	0.0007	0.0518				
20.95%	0.03%	19.71%	1.25%	0.0008	0.0611	1.18%	1.15%	0.0007	0.0526				
20.95%	0.03%	19.57%	1.38%	0.0008	0.0619	1.13%	1.10%	0.0006	0.0532				
20.96%	0.03%	19.56%	1.40%	0.0024	0.0643	1.11%	1.08%	0.0018	0.0549				
20.97%	0.03%	19.73%	1.24%	0.0007	0.0650	1.08%	1.05%	0.0006	0.0555				
20.95%	0.04%	19.51%	1.44%	0.0014	0.0664	1.01%	0.97%	0.0009	0.0564				
20.92%	0.04%	19.46%	1.46%	0.0008	0.0672	1.11%	1.07%	0.0005	0.0569				
20.95%	0.03%	19.86%	1.09%	0.0030	0.0702	1.07%	1.04%	0.0028	0.0597				
20.95%	0.03%	19.89%	1.06%	0.0006	0.0708	1.03%	1.00%	0.0006	0.0603				
20.95%	0.04%	19.89%	1.06%	0.0008	0.0716	1.01%	0.97%	0.0007	0.0610				
20.94%	0.03%	19.81%	1.13%	0.0009	0.0724	1.01%	0.98%	0.0007	0.0617				
20.95%	0.03%	19.88%	1.07%	0.0008	0.0733	0.97%	0.94%	0.0007	0.0624				
20.99%	0.03%	19.80%	1.11%	0.0013	0.0746	0.94%	0.91%	0.0011	0.0635				
20.95%	0.03%	19.80%	1.15%	0.0008	0.0754	0.94%	0.91%	0.0006	0.0641				
20.95%	0.03%	19.79%	1.16%	0.0009	0.0763	0.93%	0.90%	0.0006	0.0647				
20.95%	0.04%	19.89%	1.06%	0.0007	0.0770	0.92%	0.88%	0.0006	0.0653				
Linear estimation of cumulative O ₂ consumption from day 42 to 61													
O ₂ consumption rate (moles/day) = 0.000769													
standard error of slope = 0.000005													
coefficient of determination = 1.000													
F statistic = 21995													
regression sum of squares = 0.000084													
0.0000000 = residual sum of squares													
Linear estimation of cumulative CO ₂ consumption from day 42 to 61													
CO ₂ consumption rate (moles/day) = 0.000649													
standard error of slope = 0.000008													
coefficient of determination = 0.999													
F statistic = 7040													
0.0000001 = residual sum of squares													

All sample measurements made @ 10°C
and 1 atmosphere.

		Area 1795 Biosparging					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	1.36E+08					1.23E+08
	2-58	3.83E+07					7.30E+06
	2-46	1.66E+07					2.57E+06
	2-34	1.83E+08					2.08E+08
	2-23	1.04E+08					1.21E+07
	2-10	4.44E+06					8.05E+05
	2-0						7.68E+05
	1-TOP	3.66E+06					2.04E+06
	1-58	3.02E+07					8.51E+07
	1-46	7.24E+07					2.44E+07
	1-34	1.51E+08					1.56E+08
	1-23	1.69E+07					3.21E+07
	1-10	4.24E+06					3.27E+06
	1-0	1.73E+07					1.08E+07
Biomass (cells/g)		7.79E+08					6.69E+08

blank=no sample
or not analyzed

		Area 1795 Sparging					
Date		1 Sep	3 Sep	18 Sep	2 Oct	14 Oct	30 Oct
Time (days)		0	2	17	31	43	59
LOCATION	2-Top	5.46E+03					4.93E+03
	2-58	1.53E+03					2.92E+02
	2-46	6.66E+02					1.03E+02
	2-34	7.32E+03					8.34E+03
	2-23	4.16E+03					4.82E+02
	2-10	1.78E+02					3.22E+01
	2-0						
	1-TOP	1.47E+02					8.17E+01
	1-58	1.21E+03					3.40E+03
	1-46	2.90E+03					9.75E+02
	1-34	6.05E+03					6.24E+03
	1-23	6.78E+02					1.28E+03
	1-10	1.70E+02					1.31E+02
	1-0	6.92E+02					4.32E+02
PLFA in soil (pmole/g)		3.12E+04					2.67E+04

~ 25,000 cells/
pmole PLFA

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13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>The Department of Defense (DoD) has over 21,000 contaminated sites requiring some form of remediation. Contaminants on these sites include petroleum hydrocarbons, explosive compounds, chlorinated solvents, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls. Current technology has centered around incineration, air stripping, and the use of activated carbon. Frequently, this technology is not cost effective nor publicly acceptable. Biotreatment offers a possible alternative. Biotreatment can cost effectively eliminate contaminants and avoid the use of harsh chemicals and physical treatments. However, special care must be employed to ensure that the proper bioremediation system is designed and engineered to optimize cleanup and minimize costs.</p> <p>Gasoline Alley, Fort Drum, New York, project area is the former site of nine bulk fuel storage areas for the U.S. Army. Also included as part of Gasoline Alley is one inactive surface dump site and one inactive landfill. Historically, there existed four distinct types of fuel stored and dispensed along Gasoline Alley: unleaded gasoline, diesel fuel, kerosene, and JP-4. Throughout Gasoline Alley, there exist five distinct total petroleum hydrocarbons (TPH) plumes. This study focuses on three of the nine areas and the corresponding TPH plumes. The goals of this study were to: (a) determine potential microbial activity of Gasoline Alley subsurface soils. (b) determine Intrinsic TPH</p> <p style="text-align: right;">(continued)</p>					
15. SUBJECT TERMS Biosparging, Biotreatment, Bioventing, Contaminant, Microorganism, Radiolabeling, Total petroleum hydrocarbons					
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14. ABSTRACT (Concluded)

degradation potential of Gasoline Alley subsurface microorganisms, (c) determine parameters which will enhance subsurface microbial growth in Gasoline Alley subsurface soils, and (d) optimize parameters using column study which simulates natural subsurface conditions. To accomplish these goals, three experiments were conducted during the course of this study.

Experiment 1 determined the bioactivity potential of the subsurface soil samples. This was accomplished by adding to a series of respirometry flasks, soil sample, radio labeled acetate, nutrients, and oxygen. Experiment 2 utilized ^{14}C -Phenanthrene as a target compound for determining the likely success of bioremediation of the more recalcitrant compounds. Experiment 3 utilized a series of column tests to further determine and optimize parameters that enhance biodegradation of TPH compounds in the subsurface of Gasoline Alley soils.